THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 46, PART 6 *November* 1, 1934 NO. 257

546.59:548.73

AN X-RAY STUDY OF THE EFFECT OF HEAT ON THE STRUCTURE OF SPUTTERED FILMS OF GOLD

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ERRATUM

In "The Photoelectrons expelled from Elements by Chromium K Radiations", by H. R. Robinson, F.R.S., *Proc. Phys. Soc.*, **46**, 696 (1934), line 8, column 4, table 1

For 233·7 *read* 223·7.

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orientation phenomena. Trillat and Hirsch[||] observed a development of fibre structure on heating thin beaten leaves of platinum and gold. The present work was undertaken to investigate whether similar phenomena are exhibited by sputtered films of gold when heated, X-ray diffraction methods being employed for the purpose.

§ 2. PREPARATION OF THE GOLD FILMS

The gold films used were sputtered on thin rods of quartz about 2·5 cm. long and 0·9 mm. in diameter in an apparatus which has been described in an earlier

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[*] S. Rama Swamy, *Proc. R.S.* A, **131**, 307–20 (1931).

[†] H. Kahler, *Phys. Rev.* **18**, 210–17 (1921).

[‡] G. P. Thomson, *Proc. R.S.* A, **125**, 352 (1929).

[§] G. P. Thomson, Norman Stuart and C. A. Murison, *Proc. Phys. Soc.* **4**, 381–87 (1933).

[||] J. J. Trillat and T. v. Hirsch, *Z. f. Phys.* **75**, 784–803 (1932). See also *Comptes Rendus*, **193**, 649 (1931) and **194**, 72 (1932).

paper*. The gold plate used as the cathode was 99·99 per cent pure. The quartz rod on which the film was sputtered was provided with suitable mica rests at its ends and laid on the table provided for it in the sputtering apparatus. In order to obtain a uniform deposit of gold the rod was first sputtered on one side and then turned over and sputtered on the other side for an equal interval of time under the same conditions of pressure and applied voltage. The apparatus was evacuated with a Hyvac pump and the requisite discharge for sputtering was produced by an induction coil with a mercury interrupter connected to the 110-volt d.-c. mains. A thermionic rectifier was used in the secondary circuit. The applied potential for sputtering was of the order of 20 kV. and the current was 5 mA. The time of sputtering varied from about 20 minutes to an hour. The pressure in the apparatus, the gas in which was residual air, corresponded to a dark-space length of 5 mm. and was kept constant by a pressure-controlling device described in a note elsewhere†.

The quartz rod was thoroughly cleaned by washing first with alcohol and then with boiling conductivity water. It was dried and weighed in an assay balance to an accuracy of within 0·02 mgm. Its diameter was measured with a micrometer microscope in at least three places along its length and then it was sputtered and weighed again. This enabled the thickness of the film to be calculated to an accuracy of $0{\cdot}2 \times 10^{-5}$ cm., assuming it to be uniform. Films of varying thicknesses were obtained by sputtering for different intervals of time under the same conditions of pressure, applied voltage and current-strength. The weights and thicknesses of the gold films prepared are given in table 1.

Table 1

Number	3	5	6	7
Weight (mgm.)	0·74	0·79	0·24	0·55
Thickness (cm. × 10^{-5})	5·8	6·2	1·8	4·4

§ 3. EXPERIMENTS WITH THE FILMS

X-ray photographs of the gold films were obtained with a cylindrical Debye-Scherrer camera. A Müller X-ray tube with a copper anticathode was used and good photographs could be obtained in about 2 hours with 50 kV. and 10 mA. The heat treatment of the films consisted in maintaining them for about 4½ hours at successively higher temperatures varying from 200 to 900° C. in an electric furnace. The maximum variation of temperature for each heat treatment was about 10° C. X-ray patterns were obtained after each heat treatment. With the help of identifying-scratches made on it, the film was always kept in the same position in the Debye-Scherrer camera so that in all cases the same portions of the film produced the patterns obtained.

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* *Loc. cit.*

† S. Rama Swamy, *J. Sci. Inst.* **11**, 28–29 (1934).

After heat treatment, intensity-maxima became noticeable in the central portions of the Debye-Scherrer rings of the 111 and 222 planes, indicating that the crystals in the film were oriented with their 111 planes parallel to the surface of deposition, figure 1. These maxima were found to get smaller and better defined at higher temperatures. The Debye-Scherrer rings also grew sharper when the films were heated, thus indicating crystal growth. Film 3 was found to exhibit the orientation even before being heated. In order to place the observations on a quantitative basis the lengths L of the maxima were estimated by visual measurements and also with the help of a recording photometer. L

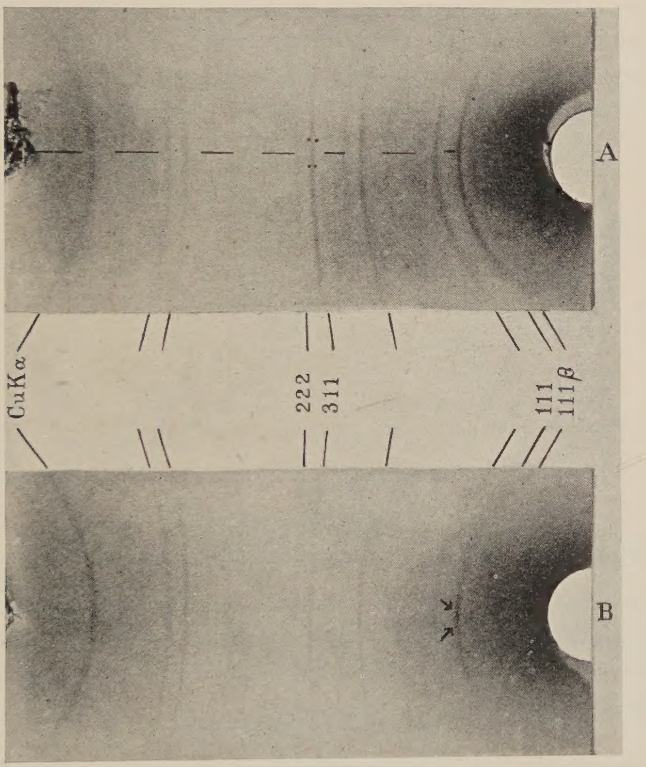

Figure 1. *A* is the Debye-Scherrer pattern of gold film no. 6 before heating. *B* is the pattern of the same film heated at 800° C. for $4\frac{1}{2}$ hours. The two arrow marks in *B* indicate the intensity-maximum observed in the 111α ring. In the original photograph the maxima in 222α and 111β are also clearly visible.

The length of the intensity-maximum indicating *perfect* orientation of the 111 planes will be the same as the diameter of the incident X-ray beam, which is assumed to be parallel. When the X-ray beam is divergent, the corresponding length will be slightly more and can be calculated from a knowledge of the divergence of the beam and the diameter of the slit used. In the camera employed this length was 1·5 mm. If L is the measured length,

$$L_0 = L - 1{\cdot}5, \qquad L_0$$

ϕ where L_0 is the length of the maximum due to orientation of the crystals. If ϕ is the angle between the Bragg plane corresponding to either end of the maximum and the surface of the film at that point, it can be shown that

$$\tan \phi = L_0/(d \sin \theta),$$

d, θ where d is the camera diameter and 2θ is the angle of diffraction corresponding to that particular Debye-Scherrer ring. The angle ϕ is a measure of the departure from perfect orientation and will be zero for perfect orientation and $\pi/2$ when orientation is absent. In figure 2 the values of ϕ obtained from the photographs are plotted against the temperatures at which the films were heated.

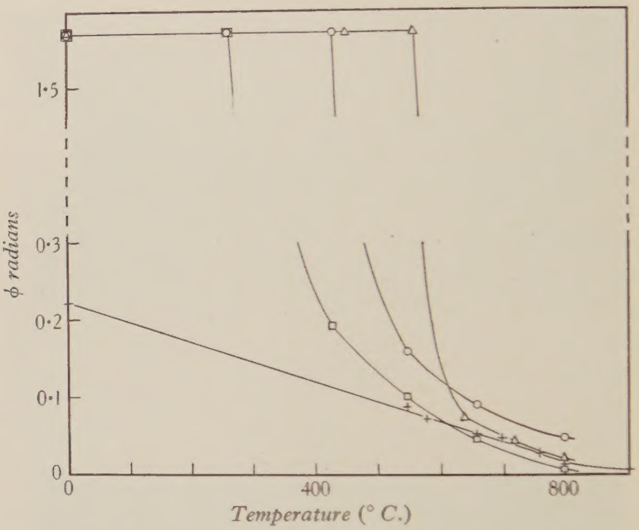

Figure 2. + Film no. 3; □ film no. 6; ○ film no. 7; △ film no. 5.

In order to study growth of the crystal when the gold films are heated, the half-intensity width of the 311 line in the photographs of films 6 and 7 was obtained
D from its photometer records. If D is the average length of the edge of the crystals taken as cubes, we have

$$B = b + k\lambda/(D \cos \theta)^*,$$

k where $k = 2\sqrt{(\pi^{-1} \log_e 2)}$

and

B B is the measured, half-intensity angular width,
2θ the angle of diffraction,
b b the part of B due to the finite size of the specimen, and
λ λ the wave-length of the X-rays used.

D will be in Ångströms if λ is in Ångströms, B and b being in angular measure. The values of D thus obtained are plotted against temperature in figure 3. The error in the measurement of the half-intensity linear width is about 0·01 mm. and so the calculated values of D are subject to an error of about 2 per cent.

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[*] R. W. G. Wyckoff, *The Structure of Crystals*, p. 376.

§ 4. DISCUSSION OF RESULTS

The orientation phenomenon has been found in all the gold films examined. The curves in figure 2 indicate that the orientation becomes noticeable at a certain temperature and becomes more perfect on further heating. The temperature at which orientation becomes noticeable is lower for the thinner films than for the thicker ones. Thus, orientation was first noticed at 430° C., 550° C. and 640° C. respectively for films of thicknesses 0·018μ, 0·044μ and 0·062μ respectively. This is possibly due to the existence of greater freedom in the thinner films, in which the crystals being farther apart than in thicker ones in which they are more closely packed. The curve for film 3, in which there was crystal orientation even before heating, is almost a straight line. Some platinum films examined by G. P. Thomson and his collaborators* exhibited a similar orientation even without being heated.

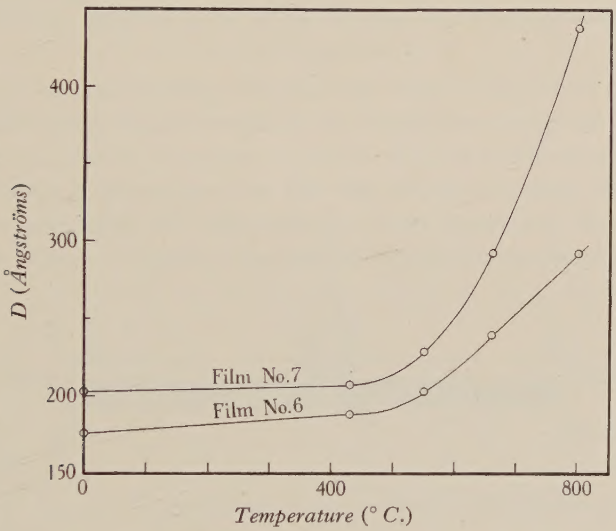

Figure 3.

The curves in figure 3 indicate that in addition to orientation there is also crystal growth when the films were heated. There is very little growth of crystals until about 400° C. But beyond this temperature they grow much faster with increase of temperature. The sizes of the crystals in films 6 and 7 are respectively 176 and 203 Å., the thicker film no. 7 containing the bigger crystals. Crystal growth is more pronounced in the thicker film than in the thinner one, the crystals being more than doubled in size at 800° C.

These two phenomena of crystal growth and orientation accompany the disintegration and consequent formation of aggregates mentioned in an earlier paper†. The lattice constant calculated from measurements of one of the photographs is

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* *Loc. cit.*

† *Loc. cit.*

$4{\cdot}07_1$ Å., which is in good agreement with the value 4·0702 found by Sachs and Weerts*.

§ 5. ACKNOWLEDGMENTS

I take this opportunity to express my deep appreciation of the helpful interest which Prof. H. E. Watson has taken in this work. I must also thank Dr K. R. Krishnaswami for the many valuable suggestions which have considerably helped in its execution. My thanks are also due to Mr N. B. Bhatt for helping me to photometer the X-ray photographs.

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* G. Sachs and J. Weerts, *Z. f. Phys.* **60**, 489 (1930). See also, Neuburger, *Z. f. Krist.* **80**, 114 (1931).

535·417

NOTE ON THE EQUALIZATION OF THE TEMPERATURES OF INTERFEROMETER TUBES

By J. J. MANLEY, M.A., D.Sc., Fellow of Magdalen College, Oxford

Received April 19, 1934.

ABSTRACT. This note is a description of two devices used for establishing and maintaining equality and uniformity of temperature for the contents of the twin tubes of Jamin interferometers. According to one method the tubes are closely wound from end to end with spirals of soft copper wire, s.w.g. 18. The other device consists of an aluminium chamber which during idle periods completely encloses the tubes. Shutters, covering the ends of the tubes, are removed prior to the carrying out of measurements.

At frequent intervals during the past two years, I have had occasion to carry out differential measurements of the continuous variations in the refractivity of benzene during intensive drying, and for the attainment of the required degree of accuracy it was imperative that the closest attention should be given to the conditions governing the temperature of the containing-tubes of the Jamin interferometer. Other workers in the field of interferometry must have experienced difficulties similar to those encountered by myself, and I believe therefore that the two devices described below will be of interest to them.

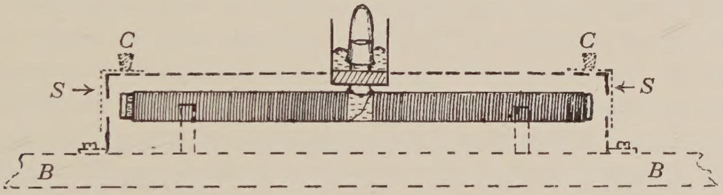

Figure 1. Note on the equalization of the temperatures of interferometer tubes.

So far as I am aware the glass tubes of an interferometer are usually placed *in situ* and left uncovered. Apparently the assumption is made that, given favourable conditions, corresponding and adjacent zones of the tubes have a common temperature; and that although the temperatures of the extremities on the left may differ from those on the right, the mean temperature of one tube is precisely equal to that of the other. Any uncertainty associated with such an assumption is, according to my experience, almost entirely removed by combining two devices which are represented in figure 1.

To the base *BB* of the interferometer is secured a rectangular aluminium chamber which in the figure is indicated by the heavier dotted lines. Apertures are provided in the lid of the chamber, as shown, for the passage of the tubulures of the interferometer tubes. The circular windows at each end of the chamber are closed by the shutters S, S when observations are not being made. These shutters are provided with cork handles C, C. The interior of the chamber is blackened and the exterior polished. Experiments prove that such a chamber, by entirely screening the tubes from local and ever active air currents as well as from radiant energy, regular or otherwise, adds quite appreciably both to constancy and to accuracy.

Uniformity and equality in the temperature of the two interferometer tubes and their contents are still further increased by enveloping the tubes with tightly fitting spirals of copper wire as shown. The wire, no. 18 s.w.g., is wound not only tightly but also so closely that successive turns have contact with each other throughout. Thus the spirals, in their power of equalizing temperatures, approach in effectiveness to cylinders of copper; indeed their efficacy may in the present instance exceed that of copper tubes, because in the case even of the most closely fitting tube contacts between it and the enclosed glass chamber must necessarily be comparatively few; whilst the spiral, by adapting itself to the irregularities of the glass surface, is in contact throughout. Hence the conductivity of heat and the attendant equalization of temperature attain maximum values.

546.212:536.632

THE EFFECT OF DISSOLVED AIR ON THE SPECIFIC HEAT OF WATER

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Received April 26, 1934 *and is revised from June* 9, 1934.

ABSTRACT. The paper describes experiments performed by the continuous-flow electric method on the specific heat of distilled water both when de-aerated and when saturated with air. The difference between the two sets of results is described and an explanation is given. The findings of other observers are critically described in the light of these experimental results.

§ 1. INTRODUCTION

In his account of experiments on the specific heat of fractions obtained from petroleum oils* the writer noted that the true specific heat could only be obtained if the liquid was thoroughly de-aerated and that when the de-aeration was not complete results higher than normal were obtained.

The results obtained by numerous observers for the specific heat of water and its variation with temperature were examined and it was found that in nearly every case they were higher in value than the results of Callendar and Barnes; moreover, the latter observers took especial care to free their water from air. It occurred to the writer that the various discrepancies might easily be accounted for by the presence of dissolved air, and the present experiments were performed to test this hypothesis.

Callendar and Barnes decided to de-aerate their water primarily in order to obtain greater steadiness of temperature, having found that the liberation of air caused a certain amount of fluctuation in the temperature-rise. Below about 50° C., however, the fluctuations are slight because the air bubbles are very small, and the writer has been able, therefore, to obtain a series of results up to this temperature with ordinary distilled water. A second series of experiments was then performed with de-aerated water to see whether any difference could be observed and also whether the results of Callendar and Barnes could be reproduced.

The accuracy claimed for the writer's results on petroleum oils was 0·2 per cent, but if the discrepancies in the specific-heat measurements were to be explained much greater accuracy was needed since the differences between the findings of various observers were only of this order.

In the following sections the methods of obtaining the additional accuracy are described. The probable error in any individual experiment was not more than 0·02 per cent, but in combining two such experiments to give a value for the specific heat the probable error was somewhat increased. In any case, the results are certainly accurate to 0·05 per cent and, where more than two rates of flow have been taken, to at least 0·03 per cent.

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* Lang and Jessel, *J. Inst. Petr. Tech.* **16**, 783 (1930); **17**, 572 (1931); **18**, 850 (1932).

§ 2. GENERAL OUTLINE OF THE METHOD

The principle of the method is to allow a stream of liquid to flow through a fine-bore glass tube, through which passes an electrically heated manganin strip, and to measure the rise in temperature arising from a steady supply of electrical energy. A very full discussion of the method has been given by Callendar and Barnes* in their classical papers on the variation of the specific heat of water with temperature.

References to the method and the apparatus used will be found in the papers of H. R. Lang† and of Lang and Jessel‡.

As frequent reference will have to be made in this paper to the work of these authors, this will be done by giving the author's name and the number of the page.

The elementary theory of the method is as follows:

E If E is the potential-difference between the ends of the heater in volts,
C C the current in amperes,
Q Q the rate of flow of liquid in grammes per second,
s s the specific heat of the liquid,
J J the mechanical equivalent of heat,
$d\theta$ $d\theta$ the rise in temperature in degrees centigrade, and
h h the rate of loss of heat in watts per degree of rise,

then when the conditions are steady the energy produced per second is

$$EC = JsQ\,d\theta + h\,d\theta \qquad \text{......(1).}$$

By changing the watts EC and the rate of flow Q in such a manner that the rise of temperature $d\theta$ is kept constant, two equations are obtained from which h can be accurately eliminated and s found. In practice it would be a long and tedious process to arrange for the values of $d\theta$ to be exactly the same in both cases, so values agreeing within 1 per cent are obtained and the equations are reduced as follows:

From equation (1)

$$Q_1X_1 = JsQ_1 + h,$$

$$Q_2X_2 = JsQ_2 + h,$$

where $$X = EC/Q\,d\theta;$$

whence $$s = (Q_1X_1 - Q_2X_2)/J\,(Q_1 - Q_2).$$

It is to be noted that h is assumed to be independent of both Q and $d\theta$; the necessary conditions for this have been carefully investigated and in these experiments great trouble has been taken to ensure that they were fulfilled; see § 8.

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* *Phil. Trans.* A, **199**, 55, 149 (1902).

† *Proc. R.S.* A, **118**, 138 (1928).

‡ *J. Inst. Petr. Tech.* **16**, 476 (1930).

§ 3. THE FLOW CIRCUITS AND CALORIMETERS

Both the liquid-flow circuit and the jacketing system were as used in the oil experiments and have been fully described by the writer. The only difference consists in the arrangement of the constant head and de-aerator and this is described in § 4. The two calorimeters used in these experiments are similar in all details, except for the size of the fine flow tube, to those described by Lang (p. 143).

The first calorimeter had a flow tube of $2\frac{1}{2}$-mm. bore and the other one of 3 mm. The method of mounting the calorimeters has been fully described by Barnes (p. 204) and his procedure was adopted in the present investigation.

§ 4. THE DE-AERATOR

The de-aerating apparatus used in the final experiments is shown diagrammatically in figure 1. It acted very efficiently indeed, for when the water jacket of the calorimeter was heated to nearly 100° C. and water from the de-aerator was allowed to flow through the calorimeter no sign of even the smallest air bubbles could be seen in the emerging water.

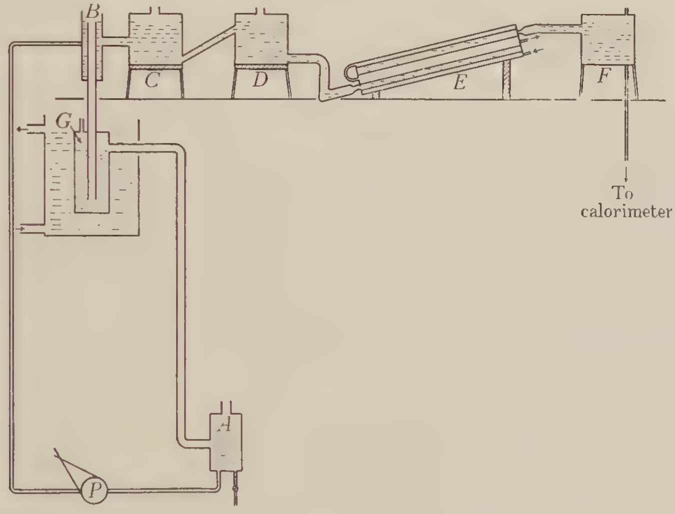

Figure 1.

Distilled water contained in the lower reservoir *A* was forced by means of a small rotary water pump into the overflow chamber *B*, which served to set the level of the water in the rest of the apparatus. This chamber was connected by a wide pipe, 1 in. in diameter, to the first heating-vessel *C*, which was a box 11 in. long, 4 in. wide and 4 in. high made from sheet copper and having a tight-fitting lid carrying three short funnels 2 in. long and $\frac{5}{8}$ in. in diameter. It was necessary to have an easy escape for the steam and the released air, otherwise the pressure set up became sufficiently great to drive the water back into the chamber *B* and so cause annoying fluctuations in head. The box rested on an electric fire element

11 in. long and 4 in. wide and capable of supplying about 1400 watts; in this chamber the water was heated to 95° C. and a great deal of air was released. The vessel *C* was connected to an exactly similar vessel *D* by means of two 1-in. tubes in parallel, water being taken off from the bottom of *C* and entering *D* just under the surface of the water. This second tank rested on a fire element which could supply about 1100 watts; in this vessel the water was completely and vigorously boiled and the remainder of the air expelled.

Water, now freed of air, was taken off from the bottom of the tank and cooled to room-temperature by flowing through the cooler *E*. This was designed to give a large surface area for cooling with the minimum restriction of flow. It consisted of three co-axial cylinders whose diameters were 1, $2\frac{1}{2}$ and 4 in. The hot water flowed through the annular space between the first two of these, while a fast stream of cold tap water passed through the smallest cylinder and also through the annular space between the last two. From the cooler the water passed into the last tank *F*, from which there was a take-off pipe to the apparatus proper; the water in this tank was covered with a layer of vacuum-pump oil to prevent contact with the air.

In order that the level of the water might be kept the same in all the tanks it was necessary to have everywhere the widest possible connecting-tubes. This caused further complications, for the hot water from *C* fed back into *B* and the overflow water became very hot; this heated the water in the reservoir *A*, which in turn heated the pump and caused it to leak badly and to function very poorly. To overcome this difficulty it was necessary to cool the overflow water. The wide overflow pipe was lead almost to the bottom of a wide cylinder *G* immersed in a large tank of cold water. When this vessel (*G*) became full, the water overflowed at the top back into the reservoir *A*. In this way it was possible to get a large area for cooling without slowing down the rate of pumping.

The interiors of the vessels *C*, *D*, *E* and *F* were all tinned with solder to prevent contamination of the pure distilled de-aerated water.

§ 5. MEASUREMENTS

Electrical measurements. The main heating circuit consisted of a battery of six 100-ampere-hour accumulators in series with an ammeter, a heavy manganin-wire standard resistance, a variable resistance board and the heater. By eliminating all rubbing contacts in the circuit it was possible to get extremely steady currents of any value up to about 5 A.

The power supplied to the heater was measured by determining the potential-difference between the ends of the standard resistance and between the ends of the heater in terms of Weston cadmium cells by means of a four-dial potentiometer. The various potential-readings were taken in rapid succession, by changing a single connecting-piece in suitably arranged mercury cups in a bakelite block.

The potentiometer was tested by taking its reading against one, two, three, four and five standard cells in turn when a 6-volt battery was connected across it.

The scale was found to be linear to at least 1 part in 5000. The standard cells were checked several times against three standard cells which had been calibrated at the National Physical Laboratory, and were found to agree with them to at least 1 part in 10,000. The value adopted in calculating the results of these experiments was

$$E = 1{\cdot}0183 - 0{\cdot}00004\,(t - 20) \text{ international volts,}$$

correction being made for temperature at each reading.

The standard resistance, which was specially designed to carry heavy currents, consisted of a coil of bare manganin wire 3 mm. in diameter, wound non-inductively on a cubical frame of bakelite of about 15 cm. side and immersed in a water-cooled oil bath. This coil was standardized against a platinum silver coil calibrated at the National Physical Laboratory. The value adopted for the calculation of the results was

$$R = 0{\cdot}9957 \pm 0{\cdot}0005\ (t - 20) \text{ international ohms,}$$

correction being made for temperature at each reading.

Thermometry. The rise in temperature of the water was measured to 0·001° C. by means of a single differential reading of a pair of platinum thermometers having a very nearly equal fundamental interval and connected to a Callendar-Griffiths bridge. The bridge was carefully calibrated both before and after the series of experiments, and the relative values of the coils did not change by more than 1 part in 5000. It should be noted that as the bridge wire had to be read to 0·05 mm. it was necessary to calibrate the bridge-wire very carefully.

The change in the value of the bridge-wire correction during the course of the experiments amounted to 1 part in 500, but is not likely to affect the first set of results (ordinary distilled water) as the experiments were performed immediately after the first calibration. In the second set of experiments the bridge-wire reading was never more than 2 cm., so that the error introduced is at most 0·004 cm. in a rise of 20 cm., which is about 1 part in 5000.

Three thermometers were used in these experiments. Thermometer A was used throughout as the outflow thermometer, as in the oil experiments. The inflow thermometer B used in those determinations gave considerable trouble owing to faulty insulation: it was repaired and used for a few of the earlier experiments, but it again gave trouble and was replaced by another thermometer E. The fundamental intervals and the ice points of these thermometers were taken before and after the series of experiments and are given in the table below, as are also the values of d determined at the end of the series. These were found from a measurement of the resistance of the thermometers in the vapour of boiling sulphur, the temperature t on the international scale being expressed by the relation

$$t = 444{\cdot}60 + 0{\cdot}0909\,(p - 760) - 0{\cdot}000048\,(p - 760)^2,$$

where p is the atmospheric pressure in mm. An iron vessel and one tin shield were used as required by the definition of the international temperature scale.

It should be noted that the change in the ice point of thermometer A has no effect on the results, since only the fundamental interval of this thermometer enters into the calculations. The constants of the inflow thermometer only enter into the calculation of the mean temperature of the experiments and the small changes noted above have no effect on the results. The values of d are higher than those usually given in text-books of physics, but the values agree favourably with those obtained by Lang for these thermometers some years ago, so they may be taken as substantially correct. No determination of d was made for thermometer B, but as this was made at the same time and with the same wire as for A the same value of d has been taken.

Table 1. Constants d of the thermometers

	Ice point (bridge units)	Fundamental interval	$d \times 10^{-4}$
Thermometer A (before)	1285·46	499·43	—
Thermometer A (after)	1284·70	499·40	1·56
Thermometer B (before)	1292·58	501·2	—
Thermometer E (before)	1283·76	499·63	1·57
Thermometer E (after)	1286·60	499·46	—

By taking differential readings before the current was switched on (cold readings), all other conditions being the same (Barnes, p. 195), corrections for conduction losses and for heat generated in the fine-flow tube by internal friction are eliminated. The only correction remaining is for the extra conduction from the outflow end of the calorimeter due to the rise in temperature. But as this increase is only 4° C. and as the end is carefully lagged, the correction must be vanishingly small.

The temperature-rise, having been obtained on the platinum scale, was reduced to the international temperature scale by means of the well-known formula

$$t - pt = d \times (t)\,(t - 100).$$

Corrections were made in the first place from the values tabulated by F. E. Hoare*, who uses a value of d equal to $1{\cdot}5 \times 10^{-4}$, and were afterwards corrected for the values of d found by experiment.

Determination of weight. At the commencement of a run the water was collected in a previously weighed flask by switching over the special two-way tap (Lang, p. 145). It was found to be impossible to adjust the stops on the two sides of the tap to give exactly the same flow, so the following procedure was adopted. About 5 minutes before the run was due to commence, a spare flask was placed under the collecting side of the tap and conditions were allowed to become steady. 15 seconds before the start the tap was switched on to the other side, the weighed flask was substituted for the spare one and at the correct instant the tap was switched back again.

Evaporation during collection was prevented by a cardboard disc placed round the nozzles of the tap and fitting tightly over the neck of the flask. Except when under the tap they were kept tightly corked. The extent of possible evaporation was examined by leaving a collecting flask uncorked for 24 hours, and the loss of weight was less than ½ gm. in a litre.

In the earlier experiments short runs were taken and flasks containing up to about 300 gm. were weighed on a chemical balance with calibrated brass weights.

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[*] *J. Sci. Inst.* **6**, 99 (1929).

In the later experiments when runs of 1000 sec. were taken about 1200 gm. were collected, and the flasks were weighed on a special large balance which was capable of detecting a change of 0·1 gm. when there was over 5000 gm. on the scale pans. The weights used were carefully scraped until they were of the correct value. A small correction was applied to reduce the weighings to those *in vacuo*.

Determination of time. For the short runs of the earlier experiments the time was recorded on a chronograph. Metal contacts were fixed to the arm of the two-way tap and to its stops, so that the time of changing over could be recorded. The chronograph drum was at the same time marked in seconds by a relay working off the pendulum of the standard clock in an adjacent astronomical laboratory. The rate of this clock was slightly variable, but the error was never more than 5 sec. in 24 hours, so that no correction had to be applied. Unfortunately the clock began, shortly after this, to give trouble by frequently stopping. As it was seen that the error in switching over and back at given signals was usually of the order of 0·1 sec. and never exceeded 0·2 sec., it was decided to take long runs of 1000 sec. and to start and stop the flow by counting the last 5 sec. with the tick of a chronometer and rapidly switching over at the given instant. An Arnold and Dent ship's chronometer was used for these time-determinations and it was rated against the broadcast Greenwich time signals. The rate was found to be constant and the error extremely small, only 2½ sec. in 24 hours. The time-measurements are not likely to be more in error than 1 part in 5000.

§ 6. PROCEDURE

The method of making an experiment has been fully described by Lang (p. 147) and was adopted in this investigation. The temperature control of the thermostat, however, was much more satisfactory, all the heaters used were electrical, and errors due to fluctuations of gas pressure were thus eliminated. It was found possible to obtain quite steady conditions at any required temperature between 0° and 100° C.

In all cases the rise of temperature of the second and third rates of flow was so adjusted as to give the same mean temperature of experiment as the first flow.

§ 7. THE X TESTS

The elementary theory of the method (p. 748) assumes that the heat-loss h per degree is independent of both $d\theta$ and Q. But this assumption will hold only so long as the flow is turbulent, i.e. so long as there is proper mixing around the thermometers and stream-line motion is absent in the calorimeter. Since this fact is of vital importance for the success of the experiments, it was thought necessary to test the point experimentally. To this end three or four rates of flow were used on various occasions and the values of X obtained plotted against the values of Q^{-1}.

Now
$$EC = JsQ\,d\theta + h\,d\theta,$$
where $d\theta$ is measured from an arbitrary zero given by the cold readings.

Then
$$\frac{EC}{Q\,d\theta} = X = Js + \frac{h}{Q}.$$

X

If then h is independent of Q throughout the range of flows used, a straight-line graph will be obtained the slope of which gives the value of h while its intercept gives the value of the specific heat in work units.

In most of the experiments with ordinary distilled water three or four rates of flow were used, and some of the X graphs are shown in figure 2. It will be seen that the points lie on the straight lines to within 1 part in 2000. The intercept was taken in these cases as the mean specific heat and the probable error was less than if only two rates of flow had been taken. The rates of flow that give turbulent motion having been determined, only two rates of flow were taken in the second set of experiments, which related to air-free distilled water.

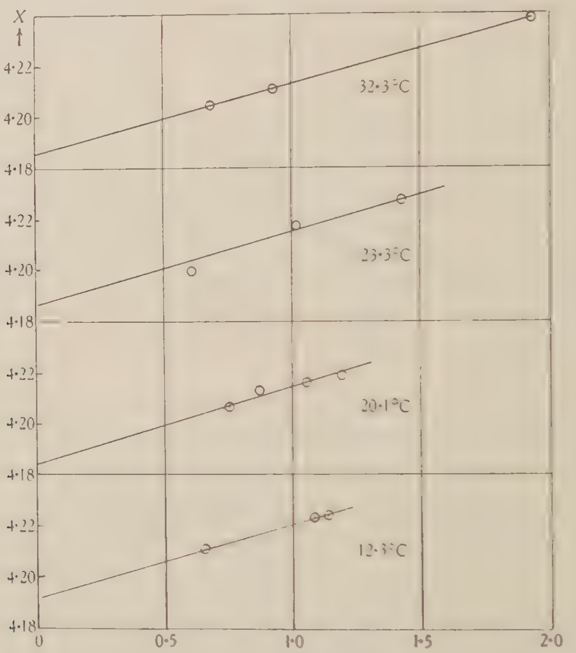

Figure 2.

Two other correcting factors may enter into the equations, one for the variation of temperature-gradient in the fine-flow tube (Callendar, p. 121) and one for the extra conduction from the outflow end of the calorimeter due to the rise in temperature. The latter correction has been regarded as negligible, an assumption which is now justified by the linearity of the X graphs.

The complete equation when corrected for the gradient in the fine-flow tube has been shown by Callendar (p. 124) to be

$$EC = JsQ\,d\theta + h_0\,(1 + h_0/xJsQ - a\,d\theta/y)\,d\theta,$$

x, y, a where x and y are constants while a is the temperature coefficient of the material of which the heater is made and in this case may be taken as zero for manganin.

Combining two such equations for two different rates of flow but the same rise of temperature $d\theta$ we get

$$\frac{E_1C_1 - E_2C_2}{d\theta\,(Q_1 - Q_2)} = Js - \frac{h_0^2}{xJsQ_1Q_2},$$

and the correction for the specific heat in work units is $h_0^2/xJsQ_1Q_2$. Further, Callendar has also shown that the value of $1/x$ is $11/25$. Taking values of 1·2 and 0·6 gm./sec. for Q_1 and Q_2, and giving h_0 the high value of 0·06 W./deg., we find that this correction amounts to only 1 part in 10,000 of the final result and so can be safely neglected.

The effect of the gradient in the fine-flow tube would be to make the X graphs slightly parabolic. Examination of the curves, however, shows that the deviations are sometimes positive and sometimes negative; so they can be put down only to accidental and not to systematic errors.

§ 8. SUMMARY OF THE OBSERVATIONS

Table 2 gives a summary of the observations. Column I gives the inflow temperature reduced from the platinum scale by means of Hoare's tables ($d = 1{\cdot}5 \times 10^{-4}$), and it is the mean of the values obtaining at the beginning and end of the run. Column II contains the mean rise of temperature, reduced as above, and is the mean of readings taken every $\frac{1}{2}$ minute during a 5-minute run, or every minute during a 16-minute run or in reality a 1000-sec. run. Column III gives the energy supplied to the heater measured in international watts, and is the mean of potentiometer readings taken every $\frac{1}{2}$ minute or every minute for runs of 5 or 16 minutes respectively. Column IV contains the value of the rate of flow of water (gm./sec.) corrected for buoyancy as already explained. Column V shows the value of X calculated from the data given in the preceding columns. Column VI gives in work units the value of the specific heat corrected for the variation in the value of d, and for the value of the international watt in absolute units. This latter correction was made by adding 4 parts in 10,000 to the results, while the correction to the international scale of temperature was obtained from a graph drawn through the values of the correction at certain fixed temperatures. Column VII gives the mean temperature of the experiment while column VIII gives the value of h in watts per degree.

The value for the specific heat of air-free water at 50·2° C. was obtained with the use of a preliminary de-aerating system which was not so efficient as that used for all the other experiments. These results are shown graphically in figure 3. The smooth graph drawn through the values for air-free distilled water is that given by Barnes and corrected as described in § 10. It will be seen that the present results agree with those of Barnes to 1 part in 2000, which is the experimental error.

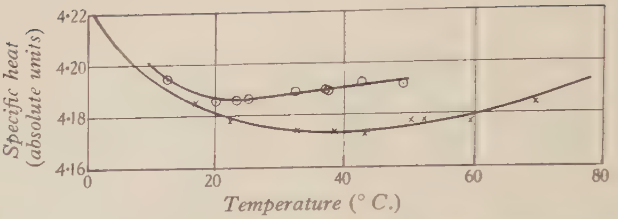

Figure 3. ⊙ ordinary distilled water; × de-aerated distilled water.

Table 2. Summary of results

Ordinary distilled water

I	II	III	IV	V	VI	VII	VIII
10·72 10·80 10·86	3·0340 3·0089 2·9915	19·267 11·147 11·461	1·5081 0·8770 0·9202	4·2111 4·2241 4·2233	4·1944	12·3	0·029
18·19 18·28 18·27 18·27	3·7563 3·6746 3·6838 3·6878	18·236 14·677 20·562 13·024	1·1522 0·9473 1·3274 0·8371	4·2134 4·2164 4·2070 4·2192	4·1857	20·1	0·031
21·54 21·56 21·60	3·4840 3·5245 3·4664	24·080 10·421 14·410	1·6457 0·6996 0·9856	4·1998 4·2275 4·2176	4·1859	23·3	0·031
23·53 23·52	3·4275 3·4263	20·008 10·424	1·3894 0·7211	4·2027 4·2193	4·1861	25·2	0·025
30·53 30·70 30·64	3·4431 3·2487 3·2642	21·111 7·141 14·794	1·4584 0·5187 1·0765	4·2041 4·2372 4·2103	4·1890	32·3	0·027
34·90 34·91 34·91 34·92	4·5516 4·5631 4·5376 4·5551	23·611 23·603 12·648 12·645	1·2346 1·2310 0·6612 0·6588	4·2018 4·2019 4·2158 4·2134	4·1893	37·1	0·018*
35·51 35·51 35·54 35·54	4·3597 4·3861 4·3481 4·3625	22·718 22·679 11·615 11·601	1·2398 1·2315 0·6345 0·6310	4·2011 4·1988 4·2102 4·2146	4·1892	37·7	0·016*
39·65 39·62	5·5837 5·7206	23·550 12·116	1·0016 0·5006	4·2107 4·2313	4·1924	42·5	0·024
46·86 46·85 46·83 46·83	4·3556 4·3820 4·3724 4·3838	23·167 23·152 8·726 8·717	1·2646 1·2558 0·4712 0·4700	4·2071 4·2061 4·2350 4·2307	4·1916	49·0	0·0201*

* Results obtained with the first calorimeter of bore 2½ mm.

Table 2 (*cont.*)

De-aerated distilled water

I	II	III	IV	V	VI	VII	VIII
14·93	3·7490	18·161	1·1458	4·2164	4·1858	16·8	0·038
14·93	3·7174	9·612	0·6091	4·2458			
20·23	3·6754	18·270	1·1817	4·2067	4·1780	22·1	0·036
20·33	3·6300	9·590	0·6341	4·2333			
31·07	3·7023	19·136	1·2265	4·2141	4·1740	32·9	0·051
31·09	3·5814	10·029	0·6591	4·2490			
36·79	3·6259	19·072	1·2496	4·2093	4·1732	38·6	0·045
36·88	3·5832	9·947	0·6543	4·2424			
41·76	3·8273	18·343	1·1384	4·2100	4·1724	43·7	0·047
41·93	3·7385	10·133	0·6394	4·2391			
42·08	3·6317	18·140	1·1869	4·2084	4·1736	43·9	0·041
42·10	3·6477	9·549	0·6173	4·2404			
48·25	4·0397	18·910	1·1070	4·2287	4·1776	50·2	0·056
48·24	3·9753	11·160	0·6570	4·2632			
50·59	3·7274	18·415	1·1707	4·2200	4·1773	52·5	0·060
50·71	3·6895	9·699	0·6175	4·2575			
57·52	3·8615	18·492	1·1364	4·2141	4·1772	59·5	0·039
57·51	3·9031	9·729	0·5868	4·2480			
68·04	3·4776	18·356	1·2468	4·2335	4·1845	69·8	0·059
67·92	3·5785	9·717	0·6346	4·2792			

§ 9. DISCUSSION OF THE RESULTS

What is called the specific heat in this paper is really the average change in the total heat per degree centigrade. This definition takes into account the fact that some of the heat is necessary to increase the vibrational energy of the molecules, and some to cause internal changes in the substance, in addition to the small part used in expanding the liquid against the constant external pressure.

The particular shape of the (specific-heat, temperature) curve of the air-free water can be explained, as suggested by Callendar, by the presence in water of a number of both ice and steam molecules. At the lower temperatures there are many ice molecules and very few steam molecules, but as the temperature rises the number of ice molecules rapidly decreases while the number of steam molecules increases. When the temperature of the substance is increased, besides the heat that must be supplied to increase the energy of the molecules, a certain amount of internal latent heat must be supplied to melt the ice molecules and a further amount to form more steam molecules.

In figure 4 (*a*) these three factors are set out in a graphical form, the abscissae representing the temperature and the ordinates the absorption of energy per degree. The natural increase of the specific heat is shown as a line of positive slope, while the curves above this represent the energy necessary to get rid of solid molecules and to form vapour molecules in solution. At 0° C. the energy required to melt the solid molecules is considerable, but as with rise of temperature the number of solid molecules present becomes less, the energy necessary to melt them becomes less and finally becomes zero. On the other hand there are practically no steam molecules present at 0° C. and so the contribution from this source is zero, but with rise of temperature the contribution to the total energy increases fairly rapidly because of the increase in the number of vapour molecules. In the uppermost curve the result of adding the ordinates at corresponding temperatures is shown, and it will be seen that the curve closely resembles the experimental one.

It must be noted that we speak of *steam molecules* in water and not of steam, for in de-aerated water bubbles of steam cannot exist. On the other hand when the water contains quantities of dissolved air the equation of a bubble of saturated air is

$$p + a/r^3 = P + 2T/r,$$

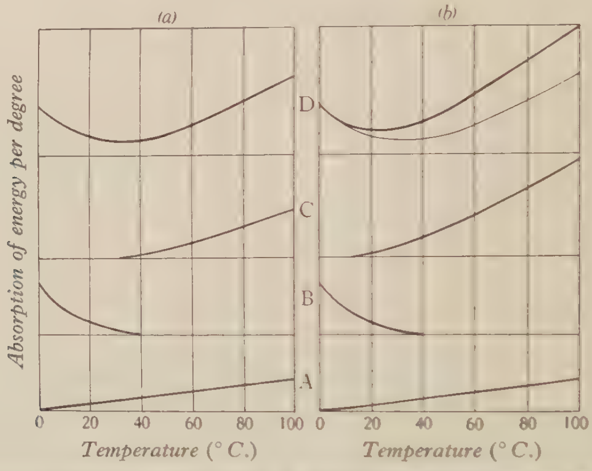

Figure 4. *A*, natural increase of specific heat; *B*, contribution of ice molecules; *C*, contribution of steam molecules; *D*, sum of *A*, *B* and *C*.

T, r, p, P

where a is a constant, T the surface tension, r the radius of the bubble and p, P the pressures outside and inside the bubble.

This is a stable condition when the radius is greater than $3a/2T$. As the temperature is raised the value of T decreases, so that the size of the smallest bubble that can remain in equilibrium in the liquid increases.

The air in the water then, will be in the form of small bubbles and these form numerous surfaces at which evaporation can take place; further, the total area of these surfaces rapidly increases as the temperature is raised.

The net effect on curve C, figure 4 (a), which shows the contribution due to vapour molecules, will be to make the curve steeper, and perhaps to make the effect of the vapour molecules reach measurable values at a lower temperature. The presence of air will not, however, have any effect on the contribution of the ice molecules or on the natural increase of the specific heat, so that the lower curves in figure 4 (b) will be the same as the corresponding curves in figure 4 (a). The resul of adding the ordinates at corresponding temperatures is again shown in the uppermost graph, and the specific heat shows higher values than in the corresponding curve in figure 4 (*a*) which is replotted in figure 4 (*b*). Further, we see that the minimum value occurs at a distinctly lower temperature.

Referring to the experimental results we see that the results for the specific heat of ordinary distilled water, which was probably saturated with air, are considerably higher than the corresponding results for air-free water, and also that whereas the minimum value for air-free water occurs at 37° C. the minimum value in the other case is at about 25° C. Our quantitative explanation appears to be on the right lines, but what seems to be most important is the fact that if *exact and reproducible results for the specific heat of water are to be obtained, air-free water must be used.* This is of the greatest importance because of the use of water as the standard calorimetric substance, and it is suggested that the calorie which is now defined as the quantity of heat required to raise the temperature of 1 gm. of water from 14·5° to 15·5° C. should for the most exact work be amended to read as the *quantity of heat required to raise the temperature of* 1 *gm. of air-free water from* 14·5° *to* 15·5° *C.*, for the difference caused by the presence of air may amount to 1 part in 1000.

Before passing on, a word or two about the heat-loss per degree as given in the last column of table 2 is perhaps necessary. It will be seen that the value of h was much higher in the case of the second calorimeter, but this is to be expected since the larger size of the bore of the fine-flow tube gives a larger surface for radiation. It will also be noticed that in the second series of experiments the heat-loss for this second calorimeter considerably increased: prior to these experiments, however, the calorimeter was taken up to over 90° C. several times in order to test various deaerating systems, and the liberation of gas occluded on the walls will account for the rise in the heat-loss. The fact that the heat-loss depends on the previous history of the calorimeter was also noticed by Barnes. It should be noted that the largest heat-loss was only 1 per cent of the heat supplied in the case of the fast flows and about 2 per cent in the case of the slow flows.

It is perhaps advisable to stress the fact that the results for the specific heat are expressed in absolute units (joules) and on the international scale of temperature.

§ 10. THE RESULTS OBTAINED BY OTHER OBSERVERS

If the results obtained by other observers are to be readily compared it is necessary to reduce them to a set of common units, and it seems obvious that we should choose absolute units (joules) and express temperature on the international scale.

Barnes was, as far as can be ascertained, the only experimenter who took the precaution of freeing the water from air. His results have to be corrected for the e.m.f. of the Clark cells (whose value he took as 1·4342 international volts) and for the international ohm. King* has shown that the e.m.f. of the Clark cells was, as Barnes suspected, 1·4325 international volts, which is equivalent to 1·4335 absolute volts. The values thus corrected are shown in the third column of table 3, Barnes's original results being given in the second column.

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* See Callendar, *Phil. Trans.* A, **212**, 8 (1912).

No correction for the temperature scale is necessary since the value of *d* was obtained on the assumption that the boiling-point of sulphur is 444·53° C., which is near enough to the value 444·60° C. on the international scale as to make no difference.

Barnes neglected to make any correction for the temperature-gradient in the fine-flow tube (shown to be negligible in the present experiments) but the correction has been carefully worked out by Callendar (p. 129) and has here been added to Barnes's results, the final corrected values being given in the last column of table 3.

Table 3. Correction of Barnes's values of specific heat of water

Temperature (° C.)	Specific heat as given by Barnes (joules)	Corrected for adjustments of electrical units	Corrected for temperature-gradient in fine-flow tube
5	4·2105	4·2045	4·2050
10	4·1979	4·1919	4·1924
15	4·1895	4·1835	4·1842
20	4·1838	4·1778	4·1786
25	4·1801	4·1741	4·1750
30	4·1780	4·1720	4·1731
35	4·1773	4·1713	4·1726
40	4·1773	4·1713	4·1727
45	4·1782	4·1722	4·1738
50	4·1798	4·1738	4·1756
55	4·1819	4·1759	4·1779
60	4·1845	4·1785	4·1807
65	4·1870	4·1810	4·1834
70	4·1898	4·1838	4·1864
75	4·1925	4·1865	4·1893
80	4·1954	4·1894	4·1921
85	4·1982	4·1922	4·1955
90	4·2010	4·1950	4·1986
95	4·2038	4·1978	4·2017

As recently as 1921 a very accurate set of determinations of the specific heat of water between 0° and 50° C. was performed by Jaegar and Steinwehr*, who used the electrical method of heating. The smallness of the rise of temperature used was not an advantage, for it meant that temperatures had to be read to 0·0002° C. and this is extremely difficult, if not impossible when the temperature is rising. Moreover, the difference between the specific heat at *t*° C. and the mean specific heat over a range of 8° or 10° C. about *t* is less than 1 part in 10,000. Thus the use of a small rise makes measurement more difficult and has no compensating advantage.

The results were expressed on the hydrogen scale, which between 0° and 100° C. is near enough to the international scale, and in terms of the international electrical standards. The corrected results are shown in table 4.

It will be seen that, except at the lowest temperatures, the results obtained by other workers are considerably higher than those obtained by Barnes, and whereas

* Jaegar and Steinwehr, *Ann. d. Physik*, **64**, 305 (1921).

Table 4. Specific heat of water according to various observers

Temperature (° C.)	Barnes	Jaegar and Steinwehr	Hercus and Laby	Rowland	Griffiths	Bousfield and Bousfield
5	4·2050	4·1987	—	—	—	—
10	4·1924	4·1918	—	4·192	—	4·1872
15	4·1842	4·1863	4·1860	4·184	4·184	—
20	4·1786	4·1821	4·1809	4·179	4·179	4·1771
25	4·1750	4·1792	—	4·176	4·175	—
30	4·1731	4·1776	—	4·173	—	4·1767
35	4·1726	4·1774	—	4·173	—	—
40	4·1727	4·1785	—	—	—	4·1832
45	4·1738	4·1803	—	—	—	—
50	4·1756	—	—	—	—	4·1936
60	4·1807	—	—	—	—	4·2049
70	4·1864	—	—	—	—	4·2143
80	4·1921	—	—	—	—	4·2188

the latter found a minimum value at 37·5° C., Jaegar and Steinwehr find it somewhere between 30° and 35° C. It is suggested that this difference is due to the presence of dissolved air in the water. Jaegar and Steinwehr's values of the specific heat are not, however, so high as those obtained for ordinary distilled water, nor is their minimum at so low a temperature. It is therefore probable that Jaegar and Steinwehr used either freshly distilled water or water that had been previously boiled so that it was in part de-aerated. It is important to note that the liberation of air in a large calorimeter of the type used by them would not affect the steadiness of the conditions, so that the accuracy of the measurement would not be diminished.

The only other recent experiments on the specific heat of water were those of Hercus and Laby[*], but these extended over only a very small range of temperature from 15° to 20° C. The results obtained were 4·1860 at 15° C., and 4·1809 at 20° C.; the accuracy claimed was 1 part in 10,000. The corresponding values of Barnes (corrected) are 4·1842 and 4·1786, the differences amounting to 5 and 6 parts respectively in 10,000. Although Hercus and Laby mention that no air was released in the apparatus, no special de-aeration was effected by them and the water must have contained small quantities of dissolved air, which would account for their higher values.

Of the older experiments probably the most accurate were those of Rowland. Day[†] restandardized his mercury thermometers and reduced the temperatures to the hydrogen scale. Some doubt must still rest upon these results, however, for it was not possible to standardize the thermometers under the experimental condition of a rapidly rising temperature. The corrected results are given in table 4.

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[*] *Phil. Trans.* A, **227**, 63 (1927).

[†] *Phil. Mag.* **46**, 1 (1898).

The agreement between the two sets of results is remarkably close. Rowland did not use de-aerated water, but violent agitation is an effective means of getting rid of air and it is probable therefore that the churning up which the water received in the calorimeter was the means of liberating a large proportion of the dissolved air. Rowland was not very certain of the minimum value at 30° C. and suggested that it might be higher, but from the results of the present experiments it seems likely that the low minimum point may have been due to the remaining quantities of dissolved air.

Griffiths* expressed his results in terms of the e.m.f. of the Clark cells (taken as 1·4342 V.), the standard ohm, and on the nitrogen scale. The true value of the e.m.f. of the cells is somewhat in doubt, for whereas Griffiths takes the value as 1·4323 V. or $1{\cdot}4330 \times 10^8$ e.m.u., Laby† suggests that their value was probably $1{\cdot}4336 \times 10^8$ e.m.u. Taking the smaller value so as to make the results as low as possible we obtain the values given in table 4, which are corrected for the electrical units and to the hydrogen scale.

It will be seen that the results are higher than those of Barnes by as much as 1 part in 1000, owing no doubt to the presence in the water of quantities of dissolved air. It is interesting to note that if the value of the Clark cells given by Laby are adopted the results agree very closely with the present values for ordinary distilled water.

The early experiments of Ludin‡ cannot be directly compared with those of the other observers so far mentioned because he used the method of mixtures and consequently was only able to obtain relative values of the specific heat of water. His results are interesting for they show a minimum value at 25° C. and a maximum value at 85° C. Between these two points the curve is very much steeper than that of Barnes but after the maximum has been reached it falls steeply until it has nearly the same value as that of Barnes at 100° C., the two curves being made to agree at 15° C.

Callendar§ has criticized these results and suggests that the drop in the curve near 100° C. can be readily explained by the slight loss of heat due to evaporation of the nearly boiling water on its way to the calorimeter. Although this may be the explanation it is by no means certainly so, for Bousfield and Bousfield‖ obtained a curve whose shape was almost identical with that of Ludin.

The Bousfields' results are shown in table 4. Above the minimum value they are much higher than those of Barnes, and the difference is greater than can be ascribed to the many possible experimental errors. The minimum value occurs at 25° C. The shape of the curve can be satisfactorily explained if we suppose that the water was, as it must have been, saturated with air. This would account for the low temperature of the minimum, and the maximum value can be explained by the fact that above 80° C. a large proportion of the dissolved air is liberated. In an open calorimeter this could easily escape without affecting the steadiness of the conditions, and the results would then tend to resume their normal values, that is to say, the curve would tend to show a decrease in the specific heat with further increase in temperature.

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* Griffiths, *Dict. App. Phys.* **1**, 490 (London, Macmillan and Co.).

† Laby, *Proc. Phys. Soc.* **38**, 169 (1926).

‡ Ludin, *Inaug. Diss. Zurich* (1895).

§ Callendar, "Bakerian Lecture," *Phil. Trans.* A, **212**, 1 (1912).

‖ Bousfield and Bousfield, *Phil. Trans.* A, **211**, 199 (1911).

The curves of Ludin and of the Bousfields are interesting in the light of the author's experiments on fractions obtained from petroleum oils. For fractions having initial boiling-points above 100° C. the (specific-heat, temperature) curves between 0° and 100° C. were all linear, but "fractions having initial boiling-points below 100° C. showed a curious bump" similar to the Ludin maximum at a temperature about 15° C. below the initial boiling-point. It was later shown that the peculiar shape was due to the presence of air or dissolved gas in the liquid, for when in later experiments better de-aeration was effected the graphs became exactly linear. There seems no doubt that the abnormal shape of the Bousfields' and Ludin's curves are due to a large extent to the presence of dissolved air.

The results obtained by the various observers mentioned in this section, except Ludin and the Bousfields, are not so high as those obtained for ordinary distilled water. It seems possible therefore that most of the observers started with freshly distilled or boiled water but took no precautions to prevent further contact with air. Only in a continuous-flow calorimeter is it possible to take this very necessary precaution. The differences found by various observers are not due to experimental errors so much as was previously supposed, but are due largely to the use by the various experimenters of substances which are not identical with one another.

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THE ELECTRICAL CONDUCTIVITY OF STRONG ELECTROLYTES AND ITS VARIATION WITH TEMPERATURE

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Received May 9, 1934.

ABSTRACT. The electrolytic conductances of potassium sulphate, potassium nitrate and sodium sulphate have been measured over a wide temperature range by means of an accurate bridge method in which alternating current is supplied by a vacuum-tube oscillatory circuit. The sensitivity and accuracy of the method have been increased by using a suitably designed amplifying circuit, and special attention has been paid to the very important question of temperature-control during the experiments.

§ 1. INTRODUCTION

The measurement of the electrical conductivity of electrolytes has attracted a great deal of attention from both physicists and physical chemists, and a large literature has accumulated round the subject. A search through the existing data, both in the standard books of physical constants(1) and in original papers, soon reveals, however, a lack of information as to the variation of this important property of solutions over a wide range of temperature.

Most investigators have satisfied themselves with a series of observations covering wide ranges of concentration at one particular temperature, generally 18° or 25° C. There are some notable exceptions such as the work of Noyes(2), Jones(3) and their collaborators who studied a number of electrolytes at temperatures as high as 306° and from 0° to 65° respectively. None of this work has been carried out, however, since the introduction of such improvements as thermionic valve oscillators giving alternating current of sinusoidal wave-form.

It was in view of this lack of data that the work was commenced at the suggestion of Prof. H. R. Robinson and Dr Allan Ferguson. S. J. Welton has already made a thorough investigation of aqueous solutions of potassium and sodium chlorides over a concentration range 0·1 N to 0·001 N at temperatures 18° and 25° to 85° C. at 5° intervals(4); the present work extends the range of the investigations to uni-bivalent salts and a further uni-univalent salt.

§ 2. EXPERIMENTAL METHOD

Bridge. In the present investigation an improved form of the Kohlrausch apparatus(5) was employed, a special Wheatstone network being assembled. A Cambridge ratio box (900–90–10–10–90–900) and a six-dial decade resistance box provided three arms of the bridge; the conductivity cell formed the fourth arm. All bridge connexions were made with lead-covered cable, the outer covering of which was earthed.

Conductivity cells. Cells of many and varied patterns have been designed, but those designed by Washburn⁽⁶⁾ were selected as being most suitable in the present case, as air is completely excluded from them. These were made of Jena 16‴ or pyrex glass and the electrodes were of stout platinum coated with platinum black.

Silence in the telephones depends on the instantaneous equality of potential at the terminals, which condition cannot be satisfied if the currents in the two branches of the bridge are out of phase. This difficulty is specially liable to arise, on account of the capacity of the cell, when one is dealing with electrolytes of high conductivity. To overcome it a variable condenser was connected in parallel with the decade box.

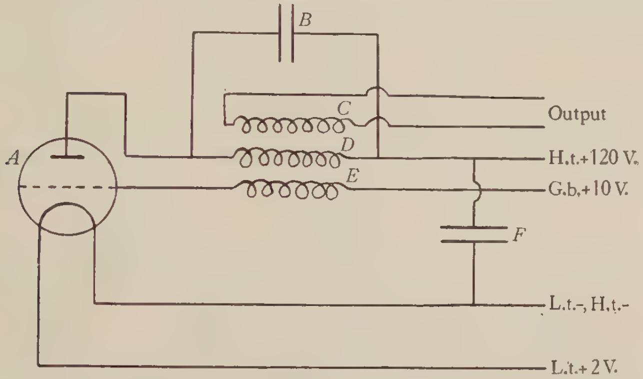

Figure 1. Oscillator. *A*, Osram P 215 valve; *B*, 0·27 mF. condenser; *C*, 1250-turn Igranic coil; *D*, 1250-turn Igranic coil; *E*, 1500-turn Igranic coil; *F*, 3-mF. condenser.

Alternating-current source. The Kohlrausch induction coil has been much used for this type of work, but the development of thermionic valve technique has led to the production of simple and entirely reliable substitutes which give a current of pure sinusoidal wave-form.

A one-valve oscillator of the tuned-anode variety was used in the present work giving a frequency of 1064 c./sec., figure 1.

Current-detector and amplifier. A pair of telephones F of the S. G. Brown type was used for the detection of the alternating current. The signals near the point of balance are generally exceedingly weak, with the result that a sharp minimum cannot be obtained. A two-stage amplifier was, therefore, inserted between the bridge and telephones, figure 2. Both the amplifier and oscillator were contained in earthed screening-boxes, and were far removed from one another.

Control and measurement of temperature. Temperature has a very appreciable influence on conductivity; the effect is about 2 per cent per degree centigrade, so that to obtain an accuracy of 0·1 per cent it is necessary to control the temperature to 0·05° C. Thus it is essential that a good thermostat should be employed. The cell was, therefore, immersed in a bath of liquid which was placed in an outer jacket, the space between these two containers being filled with wood wool. In spite of the superior properties of water as a thermostat liquid, oil was used in view of the fact that there may be disturbing electrical effects with water(7).

The temperature of the bath was controlled by a Lowry spiral regulator filled with aniline. A mercury contact operated a relay which switched the current through a 1200-watt Heatrae heater on or off. The oil was stirred vigorously by a motor-driven four-blade stirrer. This made it possible to control the temperature to within about 0·02° C.

The temperature was measured by means of a copper-constantan thermocouple in contact with the cell. In order to standardize the couple, the normal boiling-points of carbon tetrachloride, water, aniline and naphthalene were used as fixed points, the e.m.f. generated being measured on a thermocouple potentiometer reading to 1 microvolt and made by the Cambridge Scientific Instrument Co. The temperature was checked with a mercury-in-glass thermometer having a calibration certificate from the National Physical Laboratory.

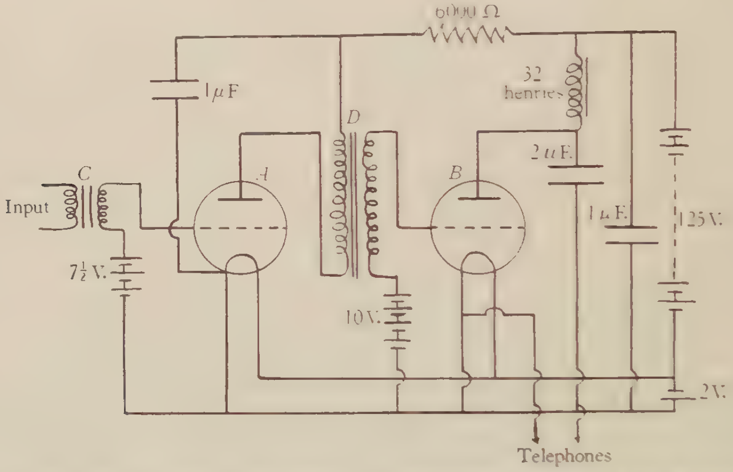

Figure 2. Amplifier. *A*, *B*, Osram P 215 valve; *C*, Varley transformer; *D*, Lotus inter-valve transformer.

Conductivity water. It is essential that the conductivity of the water used for making aqueous solutions of electrolytes should be as low as possible. A convenient and satisfactory apparatus for producing such water was described by Hartley and his collaborators(8). Ordinary laboratory distilled water is boiled in a large tinned copper vessel of about 10 litres capacity; the steam passes into a block tin condenser, and only that which condenses on the central water-cooled tin tube is allowed to pass into a 3-litre pyrex flask, from whence it is siphoned for use. Water having a conductivity of 1 or $2 \times 10^{-6}\ \Omega^{-1}$ was obtained, and this is a convenient equilibrium value(9), inasmuch as the water had been in contact with the air in the laboratory.

Solutions. The salts used, which were analytical reagents supplied by Baird and Tatlock or British Drug Houses, were recrystallized from conductivity water and thoroughly dried over phosphorus pentoxide in an air oven at 110–120° C. As sodium sulphate exists in several hydrated forms it was treated rather differently. A quantity of an anhydrous sample was carefully weighed and was heated for 4 hours at about 120° C. On cooling, it was reweighed to test for loss of water of crystallization. No loss was detected and it was concluded that the sample was anhydrous.

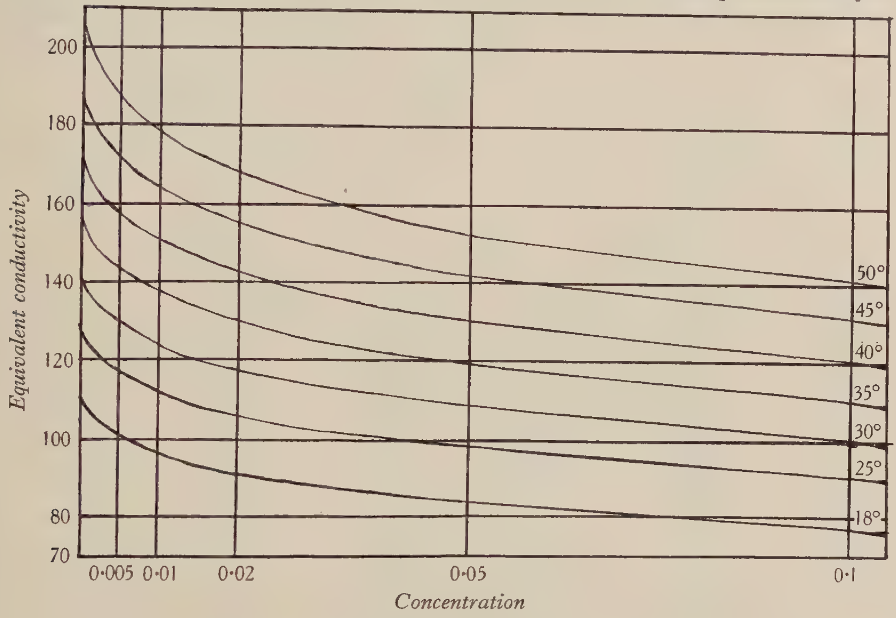

Figure 3. Equivalent conductivity of sodium sulphate.

The stronger solutions were made up by weight, the water as well as the salt being weighed. The weaker solutions were made up by diluting one of the stronger solutions. This operation was carried out in calibrated vessels. The cells were filled by means of a special pyrex flask. All glass apparatus used in preparing solutions

Table 1. Potassium sulphate 0·1 *N* (approximately). Cell type *B*

Temperature (° C.)	*R* (Ω.)	Specific conductance × 10^2	Concentration (gramme-equivalents per litre × 10^4)	Equivalent conductance
18	282·83	0·9489	1·0009	94·81
25	244·77	1·0962	0·9993	109·7
30	222·80	1·2047	0·9979	120·7
35	204·50	1·3125	0·9961	131·8
40	188·59	1·4230	0·9944	143·1
45	174·85	1·5350	0·9925	154·7
50	163·24	1·6441	0·9903	166·0
55	152·62	1·7586	0·9880	177·9
60	143·48	1·8706	0·9854	189·8
65	135·31	1·9856	0·9828	201·9
70	127·95	2·0971	0·9800	214·0
75	121·32	2·2123	0·9770	226·4
80	115·32	2·3273	0·9740	238·9
85	109·93	2·4405	0·9708	251·4

was made of pyrex glass, and was thoroughly cleaned with chromic and sulphuric acid mixture. Distilled water and, finally, conductivity water were used for rinsing, the washings being tested with blue litmus paper.

Cell constants. The cell constants were determined by filling the cells with $N/10$ potassium chloride solution containing 7·4931 gm. of salt in 1000 gm. of conductivity water⁽¹⁰⁾. Parker and Parker's results for the specific conductivity were assumed⁽¹¹⁾. It can be shown that the temperature coefficient of the cell constant is very small, the variation over the range 18–85° C. being of the order 0·06 per cent. The constant was, therefore, determined at 18° and 25° and the mean value was assumed over the whole range, 18° to 85° C.

Table 2. Equivalent conductivity of potassium sulphate

Temp. (° C.)	0·05 N	0·02 N	0·01 N	0·005 N	0·001 N
18	101·68	110·1	115·86	120·12	126·7
25	118·0	128·1	134·2	139·4	148·0
30	129·8	141·5	148·1	153·7	165·8
35	140·8	155·1	163·3	168·9	183·6
40	153·2	168·8	179·1	185·0	200·0
45	166·5	182·5	194·2	202·3	218·3
50	180·1	196·2	210·1	218·1	236·7
55	193·4	210·1	226·5	232·7	252·5
60	207·0	224·2	239·8	249·7	269·7
65	220·4	239·2	258·4	265·8	286·2
70	234·4	253·5	273·6	282·0	307·6
75	248·4	269·5	291·0	300·6	327·3
80	262·5	284·8	308·2	317·5	346·2
85	276·6	301·3	324·6	336·5	367·2

§ 3. RESULTS

The results of the investigation of potassium sulphate, potassium nitrate and sodium sulphate solutions are shown in the accompanying curves and tables. It will be observed that, for a given concentration, the conductance of a solution increases with increasing temperature in every case. This is what we should expect from the Debye-Hückel-Onsager theory⁽¹²⁾.

We have

$$L = L_0 - (\alpha L_0 + \beta)\sqrt{(2C)},$$

α, β where $\alpha = 5{\cdot}78 \times 10^5/(DT)^{\frac{3}{2}}, \qquad \beta = 58{\cdot}0/(DT)^{\frac{1}{2}}\eta,$

D D is the dielectric constant,

T T the absolute temperature,

η η the viscosity of the solvent,

L L the equivalent conductivity,

L_0 L_0 the equivalent conductivity at infinite dilution, and

C C the concentration of the solution,

and it can be shown that α and β both increase approximately linearly with temperature. Welton⁽⁴⁾ has studied potassium and sodium chlorides, and his results enable us to make a tentative calculation on the basis of the Debye-Hückel-Onsager theory. We can calculate α and β at various temperatures by consulting suitable tables for the dielectric constant and viscosity, and if we assume Welton's values for the conductance at infinite dilution at various temperatures we can calculate the conductance at any temperature and concentration. The result is shown in figure 5. At higher concentrations there is a wide difference between theory and observation, but this is not surprising as the Debye-Hückel-Onsager equation is essentially a limiting equation. For concentration $N/1000$ agreement is strikingly good although there is a deviation (not shown) which the author attributes to errors in Welton's data at higher temperatures.

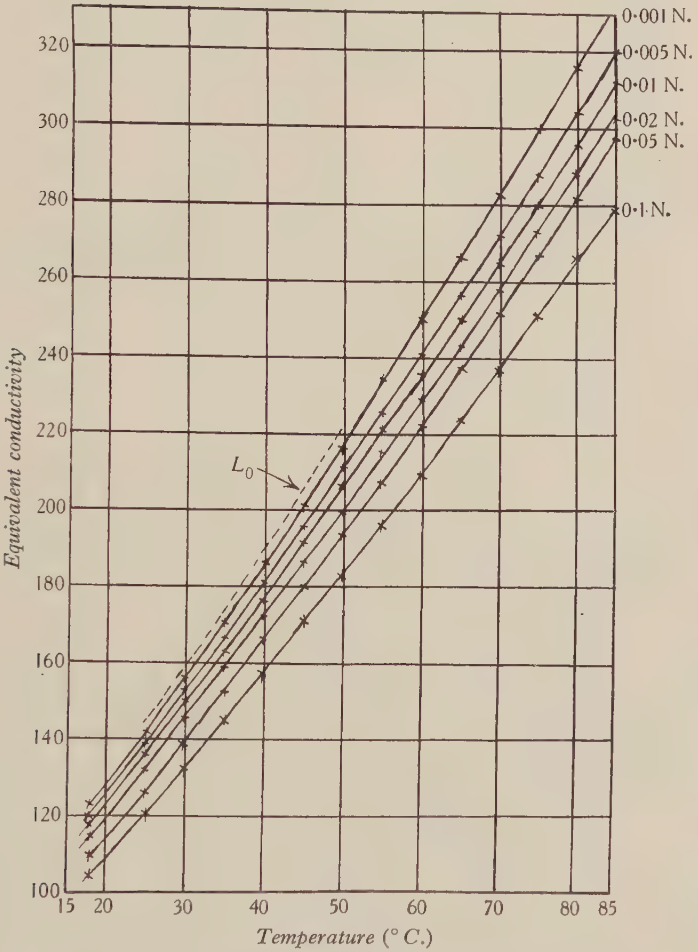

Figure 4. Equivalent conductivity of potassium nitrate.

The Debye-Hückel-Onsager theory having been shown to hold at high temperatures, it can be applied with some degree of accuracy to calculate the conductance at infinite dilution of potassium nitrate by substituting the values of the conductance for an $N/1000$ solution in the equation given above. The resulting values are shown in table 3.

Table 3. Conductance of KNO_3 at infinite dilution

Temp. °C.	25	30	35	40	45	50
L_0	144·5	159·0	173·8	189·7	205·4	221·3

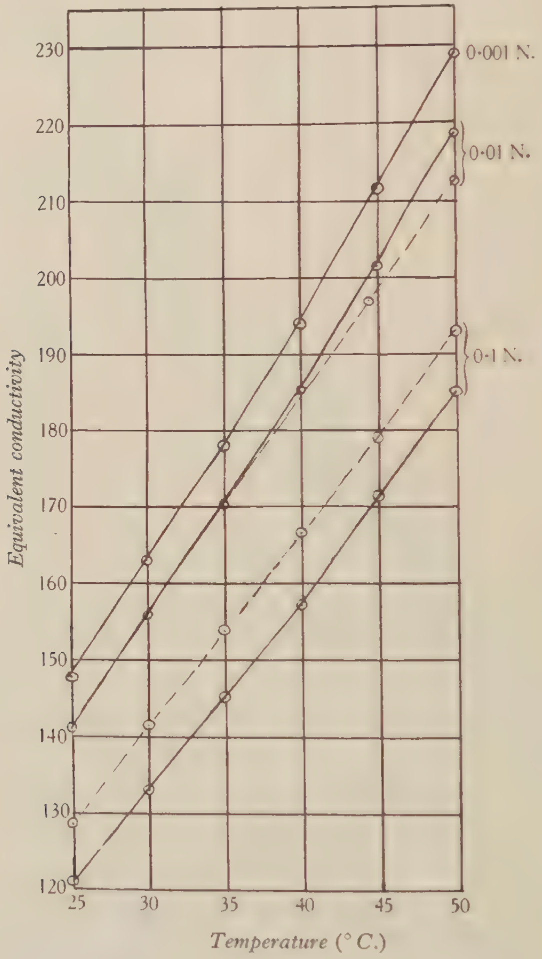

Figure 5. Equivalent conductivity of potassium chloride. ——⊙—— Debye-Hückel-Onsager theory. — —⊙— — S. J. Welton.

Unfortunately we are unable to apply the equation to the two uni-bivalent electrolytes, for it has not been put into a suitable form for application to higher-valence types.

An equation of much promise

$$L_0 = \frac{L + \beta\sqrt{(2C)}}{1 - \alpha\sqrt{(2C)}} - BC,$$

where, as before, C is the concentration and B an empirical constant, was proposed by Shedlovsky(13).

It was valid for a number of uni-univalent electrolytes up to $N/10$ and, according to Shedlovsky, seemed to hold for uni-bivalent and salts of higher valency. Subsequent investigation has shown that the equation is not applicable(14), and Shedlovsky hopes to devise an equation containing a term involving the logarithm of the concentration, predicted by Onsager.

In spite of the fact that previous workers on this subject have calculated values of the conductivity at infinite dilution the present author does not feel justified in doing so by falling back on any of the older methods of computing this constant, based on incomplete-dissociation theories such as Noyes's method(2) or purely empirical equations of the type proposed by Ferguson and Vogel(15).

§ 4. CONCLUSION

While the present investigation gives a fairly complete account of the change of electrolytic conductivity of three strong electrolytes with temperature in moderately concentrated solutions, correlation with theory is not possible until more extensive data on very dilute solutions are available. Nevertheless it seems that the Debye-Hückel-Onsager theory is fundamentally true and only requires a more rigid solution of the equations involved in the mathematical theory, or an empirical extension based on theoretical deductions. The author hopes to carry out some investigations of the conductivity of strong electrolytes in dilute solutions over a range of temperature in the near future, with an improved apparatus.

§ 5. ACKNOWLEDGMENTS

This work was carried out in the physical laboratories at East London College, and I have much pleasure in expressing my thanks to Prof. H. R. Robinson, F.R.S., for his advice and interest in the research and for the facilities which he has placed at my disposal.

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A NEW METHOD OF MEASURING THE ACOUSTICAL CONDUCTIVITIES OF ORIFICES

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Communicated by Dr E. G. Richardson, April 13, 1934.

ABSTRACT. The acoustical impedance of a tube driven by a loud-speaker is adjusted so that the acoustical pressure at a fixed point is zero. One terminating impedance is the orifice whose conductivity is required together with an adjustable tube, and from well-known impedance relations the conductivity can be calculated.

It is found that the conductivity C of a thin orifice of diameter d forming a constriction in a tube of diameter D is given by

$$C = 0{\cdot}787d/(1 - d/D)^{1{\cdot}895}.$$

When the orifices terminated the tube, the following relation was found to hold

$$C = d\,(1 - d/D)^{1{\cdot}19}.$$

§ 1. INTRODUCTION

It has long been observed that the acoustical conductivity of circular orifices placed at the end of a tube in which acoustic vibrations are being maintained is higher than that given by the classical theory. Recent work, notably that of G. W. Stewart[*] in America and E. G. Richardson[†] and E. J. Irons[‡] in England has shown that the conductivity is in some cases many times greater than that required by theory. In the case of orifices acting as constrictions in a tube no theory has been offered.

The present work deals with a new method of measuring the conductivities of orifices terminating a tube and also with those forming constrictions.

§ 2. THEORY

Z_1, Z_1' The acoustical impedance Z_1 or Z_1', defined as the ratio of alternating pressure to alternating volume-velocity, at any point P in a cylindrical tube is given by

$$Z_1 = (i \cos kl_1 . Z_2 - R \sin kl_1) \bigg/ \left(-\frac{1}{R} \sin kl_1 . Z_2 - i \cos kl_1\right) \text{[§]} \quad \ldots\ldots(1)$$

looking towards the right, figure 1, and by a similar expression

$$Z_1' = (i \cos kl_1' . Z_2 - R \sin kl_1') \bigg/ \left(-\frac{1}{R} \sin kl_1' . Z_2' - i \cos kl_1'\right)$$

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[*] *Phys. Rev.* **27**, 492 (1926).

[†] *Proc. Phys. Soc.* **40**, 206 (1928).

[‡] *Phil. Mag.* **7**, 881 (1929).

[§] Cf. Stewart and Lindsay, *Acoustics*, p. 138 (1931).

looking towards the left, where

Z_2 and Z_2' represent the terminating impedances to the right and left respectively, Z_2, Z_2'

$i^2 = -1$, i

$k = 2\pi/\lambda$, where λ is the wave-length of the sound in air, k, λ

$R = \rho c/S$, R

ρ is the density of air, ρ

S is the area of cross-section of the tube, S

c is the velocity of the sound in air, and c

l_1, l_1' are the distances from P to the terminating impedances to the right and left respectively. l_1, l_1'

It is thus seen that the impedance at point P is determined by the values of the lengths l_1 and l_1' and the end impedances Z_2 and Z_2'. If the system is driven by a loud-speaker which forms part of the impedance Z_2', a series of incident and reflected waves will be set up which, under certain circumstances, form a system of standing waves. The positions of the nodes and antinodes may be moved from point to point in the tube by altering the position or magnitude of the terminating impedances. By suitable adjustment of l_1, therefore, P may be made a place of minimum pressure.

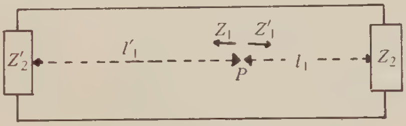

Figure 1.

If Z_2 is a rigid end and if l_1 is made equal to $n\lambda/4$, where n is any odd integer, the impedance looking to the right is zero. A microphone connected to a pressure-tube at P will record minimum sound but not necessarily silence. If the impedance Z_2' is now adjusted, it should be possible to obtain absolute silence in the telephones. Under these circumstances the impedance looking to the left also is zero.

n

On substituting an unknown impedance Z_2 in place of the rigid end and adjusting l_1 until silence is again obtained we have, from (1)

$$0 = i \cos kl_1 . Z_2 - R \sin kl_1$$

or

$$Z_2 = -iR \tan kl_1 \qquad \text{......(2).}$$

Hence Z_2 is obtained in terms of l_1.

The impedance to be measured consists of (*a*) an orifice forming a constriction in a tube, which is continued beyond the orifice to a rigid stop at a distance l_2 from it; or (*b*) an orifice terminating a tube.

l_2

In the first case the impedance consists of an orifice in series with a tube closed at one end. Hence

$$Z_2 = i\rho\omega/K - iR \cot kl_2,$$

where K is the conductivity of the orifice, ω is 2π times the frequency and $i\rho\omega/K$ is the impedance of the orifice.

K, ω

The expression $-iR\cot kl_2$ is the impedance of the closed tube, obtained from equation (1) by giving Z_2 an infinite value. Substituting in equation (2) and putting $2\pi/\lambda$ for k we get

$$2\pi\frac{S}{\lambda K}=\left[\cot\frac{2\pi l_2}{\lambda}-\tan\frac{2\pi l_1}{\lambda}\right] \qquad \text{......(3).}$$

In the second case the impedance is that due to the orifice alone; hence

$$i\rho\omega/K=-iR\tan kl_1$$

$$K=-\frac{2\pi S}{\lambda}\cot kl_1 \qquad \text{......(4).}$$

The resistances of the orifices, due to viscosity and radiation, have been neglected since the smallest orifice used had a diameter of 0·5 cm. The resistance of the tube also has been neglected. The complete impedance of an orifice is given by

$$Z=\rho\omega k/2\pi+l\,(2\mu\rho\omega)^{\frac{1}{2}}/\pi r^3+i\,[\rho\omega/K+l\,(2\mu\rho\omega)^{\frac{1}{2}}/\pi r^3]\text{*},$$

r, μ where r is the radius of the orifice and μ is the coefficient of viscosity. It is possible, therefore, to estimate the effect of the resistance. The first term is that due to radiation resistance if the sound waves emerge into free air, the second term is the resistance due to viscosity and the last two terms are the reactance components. At a frequency of 1000 c. sec. and for an orifice 0·5 cm. in diameter and 0·158 cm. long, we find the following values:

$$\frac{\text{Viscosity term}}{\text{Total reactance}}=0{\cdot}85\text{ per cent}$$

$$\frac{\text{Total resistance}}{\text{Total reactance}}=1{\cdot}87\text{ per cent.}$$

Where the orifice forms a constriction in the tube, the radiation resistance is absent and the latter ratio becomes 0·85 per cent. Since the viscosity resistance increases with frequency, a limiting frequency can be calculated above which it is not permissible to neglect the resistance.

§ 3. APPARATUS

Figures 2 and 3 show the apparatus used. A metal diaphragm loud-speaker L, driven by a valve oscillator and amplifier, is attached to one end of a brass tube 2 in. in internal diameter and about 18 in. long. At the other end is attached a brass connecting-piece C fitted with a short length of copper tube T called the "pressure-tube." This protrudes into the main tube and is bent so that the opening lies on and perpendicular to the axis of the main tube. Thus the position of the opening relative to any point in the tube can be accurately known. The faces of the connecting-piece are each capable of moving through about $\frac{3}{8}$ in. in a direction parallel to the axis but may be pressed back towards the main body of the connector against the tension of three spiral springs, as shown in figure 3. In virtue of this arrangement the main tube can be extended by a similar 2-in. tube or any other apparatus whose impedance is required. The extension from the main tube is fitted with a massive brass piston *A* which can be moved to any position relative to the pressure-tube, the exact distance being measured by a metre stick *M* and the vernier *V* attached to the piston-handle. The piston consists of a solid brass cylinder 2 in. long having a $\frac{1}{4}$-in. leather washer and a $\frac{1}{8}$-in. brass plate at each end. It makes a good fit in the tube and side play is absent. Its impedance is therefore taken to be infinite. The pressure-tube communicates by means of a short length of rubber tubing with a telephone ear-piece acting as a microphone. It is placed in a metal box packed with cotton wool and mounted on rubber supports so that it is insulated from outside sound. The output is amplified by a 4-valve amplifier and is listened to in head telephones. Similarly the loud-speaker is placed inside a metal box and cotton wool and felt are packed round it. Attached to the main tube near the loud-speaker are two side tubes; one $\frac{5}{8}$ in. in diameter, is fitted with a piston *B*, and the other, *D*, is $\frac{1}{8}$ in. in diameter and allows the pressure inside the tube to be restored to normal after any movement of pistons *A* or *B*.

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* Cf. Stewart and Lindsay, *Acoustics*, p. 120 (1931).

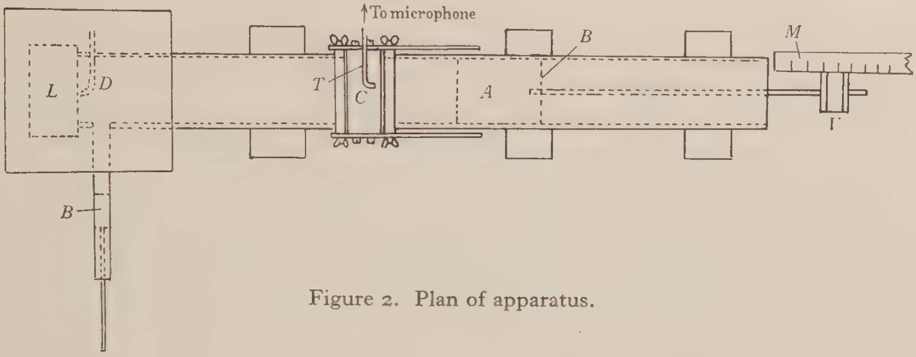

Figure 2. Plan of apparatus.

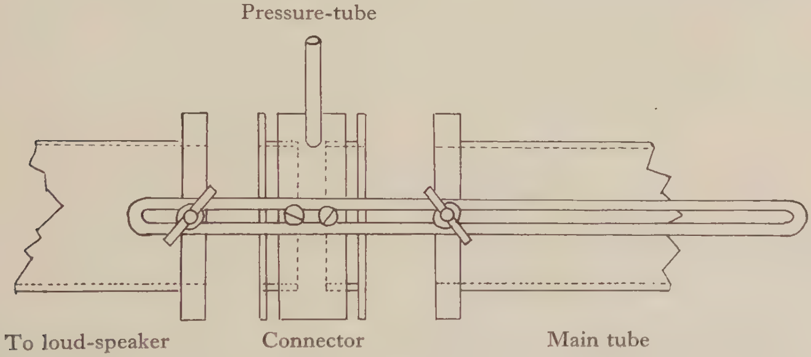

Figure 3. Detail of the connecting-piece showing the method of attachment to the main tube.

The effect of the pressure-tube on the vibrations in the main tube was determined by separating the tubes at the connector as shown in figure 3, and using the main tube as a simple resonator excited by an external loud-speaker. Piston *A* was adjusted to give silence in a second microphone placed near the opening. It was found that the introduction of the pressure-tube at any point in the main tube made no difference to the silence point; nor did altering the length of the rubber connexion from the pressure-tube to the microphone. Since the areas of the main tube and the pressure-tube were in the ratio of 256 : 1 little effect would be expected. From this it is seen that the pressure-tube and associated microphone were analogous to a voltmeter in an electrical circuit.

§ 4. PROCEDURE

In performing the experiment at any frequency, the apparatus was arranged as shown in figure 2 and piston A was moved through three or four successive positions of minimum sound in the headphones. These positions were noted and the wave-length of the sound was found by difference. The piston was now set at a distance of $\lambda/4$ cm. from the pressure-tube and piston B was adjusted to give silence in the head telephones. The impedance at the pressure-tube was therefore zero. It was found that the position of the piston B was rather critical, a movement of less than 1 mm. being sufficient to pass through a minimum. This adjustment had to be made for each frequency whether the orifices were to be measured in the tube or at the end of it.

Orifice within the tube. For this case the experimental orifice was inserted between the connecting-piece and the main tube and the piston A was adjusted to give silence once more. Three or four successive positions, differing by $\lambda/2$ from each other, were found so that the wave-length could be calculated. The experiments were repeated with the orifices moved to greater distances from the pressure-tube. This was effected by inserting a series of distance pieces, and a set of these was made up whereby l_1 could be increased to 8·75 in. in steps of 0·125 in.. Table 1 shows a typical set of results.

Table 1. A typical set of results

Diameter d of orifices (cm.)	Measured lengths l_2 (cm.)	$\lambda/2$ (cm.)	kl_2	cot kl_2	$\frac{2\pi S}{\lambda K}$	K
4·0	10·93 27·75 44·60	16·82 16·85	− 1·0976	− 0·5120	0·0752	50·3
3·5	10·44 27·92 43·98	16·85 16·69	− 1·1892	− 0·4013	0·1859	20·3
3·0	9·58 26·46 43·27	16·88 16·81	− 1·3502	− 0·2243	0·3629	10·7
2·5	8·19 25·02 41·46	16·83 16·44	+ 1·5316	+ 0·0392	0·6264	6·03
2·0	6·02 22·83 39·56	16·81 16·73	+ 1·1258	+ 0·4769	1·064	3·55
1·5	3·50 20·35 37·08	16·85 16·73	+ 0·8499	+ 0·8892	1·476	2·56
1·0	1·60 18·46 35·43	16·86 16·97	+ 0·2992	+ 3·242	3·829	0·986
0·5	0·46 17·34 34·16	16·88 16·82	+ 0·0860	+ 11·57	12·16	0·311

$l_1 = 13\cdot96$ cm.; $kl_1 = -0\cdot5309$; tan $kl_1 = -0\cdot5872$; mean of $\lambda/2 = 16\cdot86$ cm.; temperature 14·3° C.; $S = 20\cdot2$ cm^2; K is calculated from equation (3).

The conductivities of the orifices were obtained from equation (3) by plotting cot $2\pi l_2/\lambda$ against tan $2\pi l_1/\lambda$. The intercepts on each axis gave the values of $2\pi S/\lambda K$, from which K was calculated. It will be seen from figure 4 that the points lie on a straight line except for large values of cot $2\pi l_2/\lambda$ and tan $2\pi l_1/\lambda$; for these the method ceases to be accurate.

These facts are illustrated in figure 5 where the conductivity is plotted against the distance l_1 of the pressure-tube from the orifice. When l_1 is small, i.e. when the orifice is at what corresponds to the first antinode, an abnormally large conductivity is obtained, which does not appear at the second antinode. This is due to the disturbed conditions in the neighbourhood of the constriction, since the conductivity reaches a constant figure when the pressure-tube is about 1·9 cm. away. The intensity of the sound-waves was kept very small in an attempt to avoid vortex motion near the orifice, and reliance was placed on high amplification of the microphone output to increase the sensitivity. It was quite impossible to hear any sound from the tube by the ear alone when the tube was working.

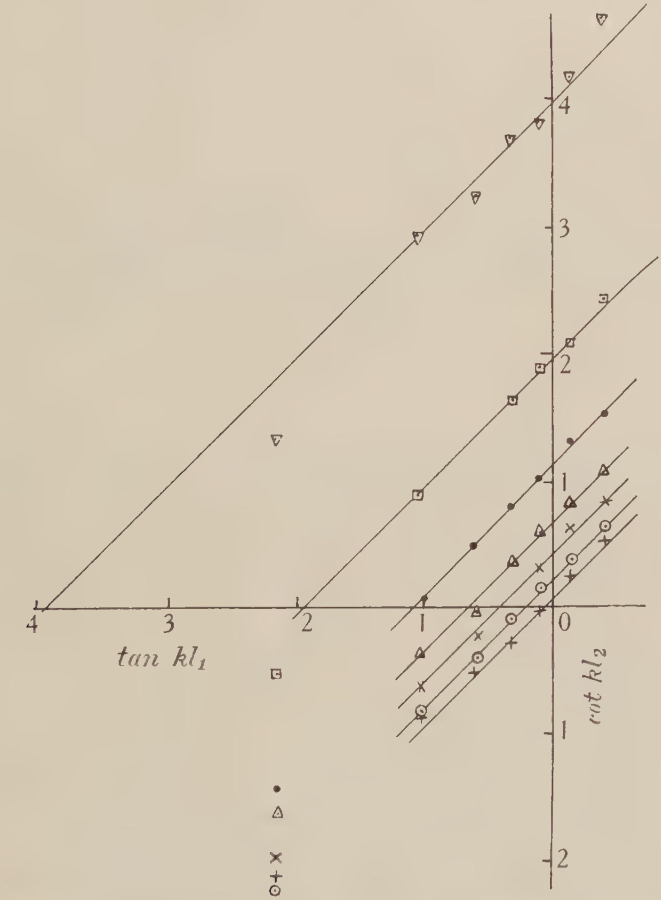

Figure 4. Orifices as constrictions in a tube. Graphs of tan kl_1 against cot kl_2 for the second position of piston *A* to give minimum audibility. $\frac{1}{2}\lambda = 16{\cdot}86$ cm.

An attempt was made to explore the shape of the wave-fronts close to the orifice by repeating the readings with the pressure-tube displaced from the axis.

The results are shown in figure 6 which shows that the wave-fronts become plane at about 1·9 cm. from the orifice, since the value of l_2 remains constant for any displacement of the pressure-tube along a radius. The graph also shows that for a maximum displacement of the pressure-tube the variation of l_2 with l_1 is smaller than that when the displacement is zero. It appears, therefore, that the wave-fronts become almost plane at the sides of the tube within a much less distance from the orifice than they do at the centre.

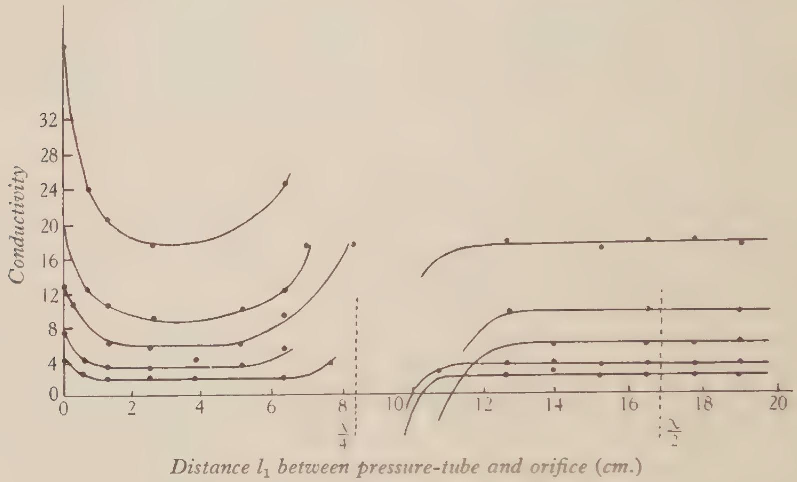

Figure 5.

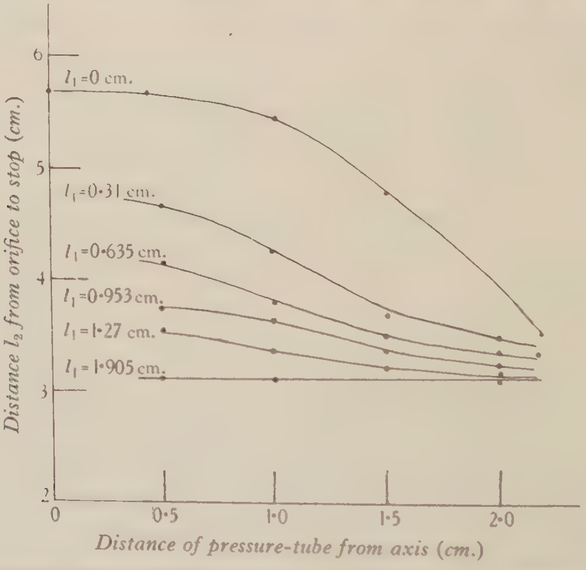

Figure 6. Graph showing the position of minimum audibility plotted against the displacement of the pressure-tube from the axis. Diameter of orifice 2·0 cm. Length 0·158 cm. $\frac{1}{2}\lambda$ 16·86 cm.

The measured conductivities have been reduced to those for an orifice in an infinitely thin plate by the following well-known relation:

$$\frac{1}{K}=\frac{1}{C}+\frac{1}{A/L} \qquad \text{......(5),}$$ [*]

where C is the conductivity in an infinitely thin plate,

A the area of the orifice, and

L the length of the orifice.

Table 2 shows this reduction from K calculated from the intercepts on figure 4. In figure 7, the ratio d/D, where d is the diameter of the orifice and D that of the tube, is plotted against C, curve (1). Curve (2) shows results obtained by Irons[†] by a Kundt's-tube method, assuming that the orifices referred to in his paper were 2 mm. long.

Table 2. Orifices in a tube 5·08 cm. in diameter

Diameter d of orifices (cm.)	$\frac{d}{D}$	Intercept from figure 4, $2\pi S/k\lambda$	K	$\frac{1}{K}$	$\frac{L}{A}$	$\frac{1}{C}$	Conductivity	
							measured	calculated from equation (6)
4·0	0·7910	0·105	35·85	0·02797	0·01254	0·0154	64·9	60·9
3·5	0·6920	0·226	16·63	0·06013	0·01642	0·04371	22·88	25·61
3·0	0·5930	0·423	9·74	0·1027	0·02240	0·08030	12·45	12·96
2·5	0·492	0·660	5·71	0·1751	0·0378	0·1373	7·28	7·16
2·0	0·395	1·09	3·45	0·2899	0·0503	0·2396	4·17	4·08
1·5	0·296	1·93	1·95	0·5128	0·0894	0·4234	2·36	2·30
1·0	0·1976	3·93	0·958	1·044	0·2012	0·8426	1·19	1·19

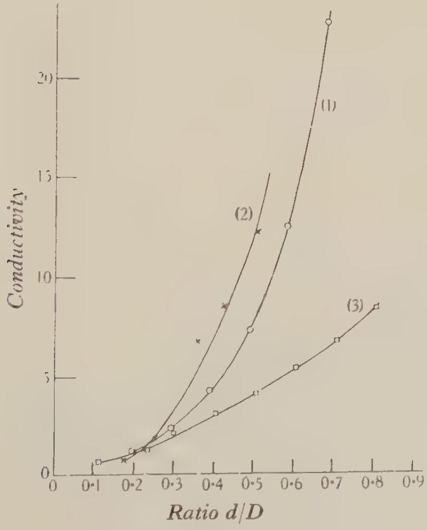

Figure 7. Curve (1), orifice forming a constriction; curve (2), Irons's results; curve (3), orifice terminating a tube.

[*] Cf. Rayleigh, *Sound*, 2, 181 (1896).

[*] *Loc. cit.*

The conductivity was assumed to depend upon the ratio of the diameters of the orifice and the tube and also on the diameter of the orifice separately, since for very small ratios of d/D the conductivity should approximate to that calculated by Rayleigh, namely d. For large orifices the conductivity should be very great and finally become infinite when $d = D$. These conditions are fulfilled by an equation of the type

$$C = \alpha d/(1 - d/D)^{\beta} \qquad \text{......(6),}$$

α, β where α and β are constants.

From curve (1), figure 7, the values obtained were

$$\alpha = 0{\cdot}787 \quad \text{and} \quad \beta = 1{\cdot}895.$$

The last column in table 2 shows C calculated from equation (6) while the experimental values are given in the adjacent column.

The classical theory according to Rayleigh requires that $\alpha = 1$, but he assumed that the incident wave was plane and the emergent wave hemispherical. These conditions are only approximately fulfilled in the case of a constriction in a tube, as we can see by considering the velocity-potential on each side of the orifice. On the side facing the loud-speaker it is due to (i) the incident plane waves from the loud-speaker, (ii) the waves reflected from the surrounds of the orifice, and (iii) the part of the incident waves which have been transmitted through the orifice, reflected from the rigid stop, and once more transmitted through the orifice. The latter is an approximately hemispherical component. Similarly the velocity-potential on the opposite side of the orifice consists of one hemispherical and two plane components.

Orifice at the end of the tube. In order to measure the conductivities of orifices terminating a tube, the preliminary adjustments of piston B were carried out with piston A at a distance $\lambda/4$ from the pressure-tube. The main tube was then replaced by a telescopic tube with a flange on the end of the movable portion, to which the orifices were bolted. The length l_1 was varied until silence or a minimum sound was obtained in the head telephones. A baffle 5 ft. square surrounded the orifices.

§ 5. RESULTS

The results were calculated from equation (4) and are shown in table 3 for several different frequencies. The measured conductivities were reduced to what they would be in an infinitely thin plate and plotted against the ratio of the diameters of the orifice and tube; see curve (3), figure 7.

As before, it was assumed that the conductivity of the terminating orifice was given by $C = f(d, d/D)$. The end conditions are somewhat different from those in the preceding case, since when $d/D = 1$ the conductivity should be approximately twice the diameter. When d is small the conductivity should reduce to d. These conditions lead to an equation of the type

$$C = \alpha' d\,(1 + d/D)^{\beta'} \qquad \text{......(7),}$$

α', β' where α' and β' are constants.

Table 3. Measured conductivities of orifices at the end of a tube at different frequencies

Diameter of orifices (cm.)	Conductivities of orifices at frequencies of				Mean K
	875	912	1000	1160 c./sec.	
4·0	6·35	6·93	7·5	7·98	7·20
3·5	5·53	5·52	5·68	6·18	5·73
3·0	4·20	4·41	4·22	4·98	4·45
2·5	3·12	3·19	3·67	3·61	3·40
2·0	2·21	2·51	2·85	2·40	2·49
1·5	1·54	1·72	1·95	1·70	1·73
1·6	0·90	1·04	1·10	1·04	1·02

From curve (3), figure 7, it was found that

$$\alpha' = 1 \quad \text{and} \quad \beta' = 1{\cdot}19.$$

Table 4 shows the agreement between the measured conductivities and those calculated from equation (7). It is seen that for small orifices this equation reduces to the classical value, the conditions being exactly those assumed by Rayleigh. For large orifices, however, the equation gives higher values than those calculated theoretically. In column 6 of table 4 are tabulated the conductivities calculated from an expression proposed by A. E. Bate*, viz.

$$C = d.2^{d/D} \qquad \ldots\ldots(8).$$

Table 4. Conductivities of orifices terminating a tube reduced to thin plate

Diameter of orifices (cm.)	$\frac{d}{D}$	K	Conductivity		
			reduced for thin plate	from equation (7)	from equation (8)
4·0	0·813	7·20	8·38	8·10	7·02
3·5	0·712	5·73	6·67	6·64	5·73
3·0	0·610	4·45	5·30	5·29	4·58
2·5	0·508	3·40	4·05	3·98	3·56
2·0	0·407	2·49	3·04	3·00	2·65
1·5	0·305	1·73	2·08	2·06	1·86
1·0	0·203	1·02	1·28	1·28	1·18

Measurements on long orifices. Measurements were made on an orifice 1·89 cm. in diameter and of length which could be increased from $\frac{1}{8}$ in. to $\frac{10}{8}$ in. in steps of $\frac{1}{8}$ in. The results are plotted on figure 8, curve (1) being the measured conductivity and curve (2) the values reduced by equation (5) to those for an infinitely thin plate. The value obtained from equation (6) is 3·59 whereas the maximum value on curve (2) is 3·11. For a long orifice forming a constriction in a tube it appears, therefore, that L in equation (5) needs to be greater than the actual length in order to give an adequate correction. In this connexion it is interesting to note that G. W. Stewart*, in an experiment on the transmission ratio of a tube having a Helmholtz resonator as a side branch, had to take the conductivity of the orifice as being that of one six times the length in order to make his results agree with the theoretical transmission ratio.

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* *Phil. Mag.* **10**, 624 (1930).

Curves (3) and (4) on figure 8 show the results of measurements made on an orifice 2·5 cm. in diameter placed at the end of a tube. The lengths were increased from 0·125 to 1·91 cm. Curve (3) shows the measured conductivity while curve (4) shows the conductivities reduced to infinite thinness. In this case the "corrected" value of 3·95 agrees well with that calculated from equation (7), viz. 4·05.

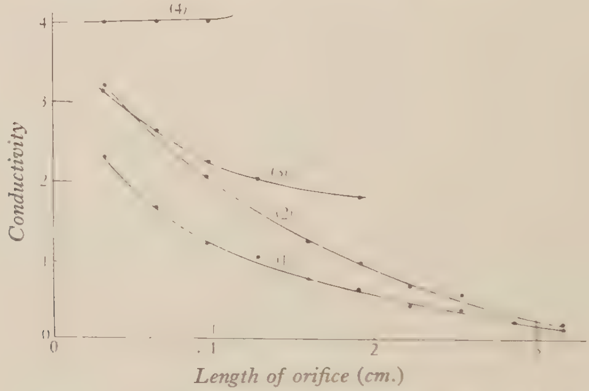

Figure 8. Effect of the length of an orifice on the conductivity. Curves (1) and (2), measured and corrected conductivities of an orifice in a tube when $\frac{1}{2}\lambda = 8{\cdot}98$ cm.; curves (3) and (4), measured and corrected conductivities of an orifice at the end of a tube when $\frac{1}{2}\lambda = 18{\cdot}11$ cm.

§ 6. CONCLUSION

Further experiments are being made on the conductivities of short lengths of tubes placed as constrictions and as side branches in a tube. It is also proposed to apply the method to measure the conductivity at the junction of two tubes of different areas. The method is not restricted to the measurement of conductivities, however, for it may be used equally well to measure the impedance of acoustical horns, telephone ear-caps, and microphone mouth-pieces, etc. when the resistance is small and when there are no reflected waves coming from the unknown impedance back into the tube. If there were such waves, as there would be if a Helmholtz resonator were attached at the orifice to the tube, the conductivity of the orifice would be considerably modified by the presence of the tube. Hence the measured impedance would not be that of the resonator in free space.

§ 7. ACKNOWLEDGMENTS

My thanks are due to Prof. G. P. Thomson for facilities to carry out this research and to Dr E. G. Richardson for his helpful advice and criticism.

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* Stewart and Lindsay, *Acoustics*, p. 120 (1931).

537·746

A BRIDGE FOR THE DETERMINATION OF THE FREQUENCY OF AN ALTERNATING CURRENT IN THE AUDIO-FREQUENCY RANGE

By GEOFFREY D. PEGLER, B.Sc.

Received May 17, 1934.

ABSTRACT. When the secondary of an air-cored transformer, of inductance N, is closed through a total resistance Q, the effective resistance P' and the effective inductance L' of the primary are given by

$$(P' - P) = p^2M^2Q/(Q^2 + p^2N^2),$$
$$(L - L') = p^2M^2N/(Q^2 + p^2N^2),$$

where M is the mutual inductance between primary and secondary, and p is 2π times the frequency.

If Q is varied and p is kept constant, P' becomes a maximum when $Q = pN$, and under this condition

$$(P' - P)_{\text{max.}} = pM^2/2N,$$

which is proportional to the frequency,

while $$(L - L')_{\text{max.}} = M^2/2N = \text{a constant.}$$

The above equations form the basis of the proposed method of determination of frequency, the maximum change in P corresponding to any frequency being measured by the Owen a.-c. bridge. The changes of resistance necessary to satisfy the third of the above equations may be effected with a single control, since both $(P' - P)_{\text{max.}}$ and the corresponding value of Q are proportional to the frequency. The change required to satisfy the last equation is effected by the mere closing of a switch. The effect of residuals is discussed also.

§ 1. INTRODUCTION

The principle of this bridge depends on the changes in effective resistance and inductance of the primary coil of an air-cored transformer as the resistance of the secondary circuit is varied. These changes may be measured with any suitable bridge, the Owen bridge being chosen because it is easily adjusted owing to the independence of its balance conditions, and because a Wagner earthing arrangement can very simply be included in it. The method dispenses with the necessity for knowing the absolute resistance of the primary coil or its variation with frequency and temperature, and gives a linear relationship between the frequency and a measured resistance.

§ 2. THEORY OF THE METHOD

If an alternating voltage be applied to the ends of the primary of two adjacent coils, then when the circuit of the secondary is closed the effective resistance of the primary rises and its inductance falls, as shown in the equations:

$$P' - P = p^2M^2Q/(Q^2 + p^2N^2) \qquad \text{......(1)},$$

$$L - L' = p^2M^2N/(Q^2 + p^2N^2) \qquad \text{......(2)},$$

P, L
P', L'
Q, M

where P and L respectively denote the resistance and inductance of the primary when the secondary circuit is open, and P' and L' their effective values when the secondary circuit is closed through a total resistance Q; M denotes the mutual inductance between primary and secondary, N the inductance of the secondary, and $p = 2\pi f$, where f is the required frequency of the supply.

It is easily shown that, at any given frequency, P' becomes a maximum when the following condition is satisfied,

$$Q = pN \qquad \text{......(3)}.$$

Under this condition equations (1) and (2) reduce to

$$\boldsymbol{(P' - P)_{\text{max.}} = pM^2/2N = f \times \textbf{a constant}} \qquad \text{......(4)},$$

$$\boldsymbol{(L - L')_{\text{max.}} = M^2/2N = \textbf{a constant}} \qquad \text{......(5)}.$$

The maximum increase in P is thus simply proportional to the frequency, whilst the simultaneous decrease of L corresponding to this maximum value is independent of the frequency. These simple relations form the basis of the method of frequency-determination now proposed, and we may rewrite (4) in the form

$$\text{frequency } f = k\,(P' - P)_{\text{max.}} \qquad \text{......(4}a\text{)}.$$

The Owen bridge for the determination of self-inductance in terms of capacity and resistance lends itself very conveniently to the required measurement of the maximum increase in P and has accordingly been adopted.

The frequency is obtained to a close approximation by multiplying the increase in P by a constant which can be obtained initially by a simple calibration experiment at a single known frequency. The coil L, P is placed in the inductance arm of the bridge, the arrangement of which, with the symbols employed, is indicated in figure 1.

When the bridge is balanced, first with the secondary open, then with the secondary closed, the condition $Q = pN$ being attained, we have

$$L = R_1K_3r,$$

$$L' = R_1K_3r',$$

so that $$(L - L')_{\text{max.}} = M^2/2N = R_1K_3\,(r - r') = \text{a constant} \qquad \text{......(6)}.$$

Thus it is seen that $(r - r')$ has always the same value, independent of the frequency.

The second condition to be satisfied in order that the bridge may be balanced is

$$R_2 = R_1K_3/K_4 = \text{a constant} \qquad \text{......(7)}.$$

Since R_1 and K_3/K_4 remain constant at all frequencies, we may conveniently divide the arm AB into two portions, the first consisting of the primary coil and a small variable resistance for adjusting the balance when the secondary is open, and the second consisting of a variable non-inductive resistance box S set always at the same value S_0 for the balance on open secondary. The increase $(P' - P)_{\text{max.}}$ is then equal to the decrease $(S_0 - S)$ required to compensate this and so maintain condition (7). Thus only two balances are necessary for each frequency, one with the secondary circuit open, and the other with the secondary circuit closed and with the resistance in the arm BC diminished by the amount indicated in equation (6).

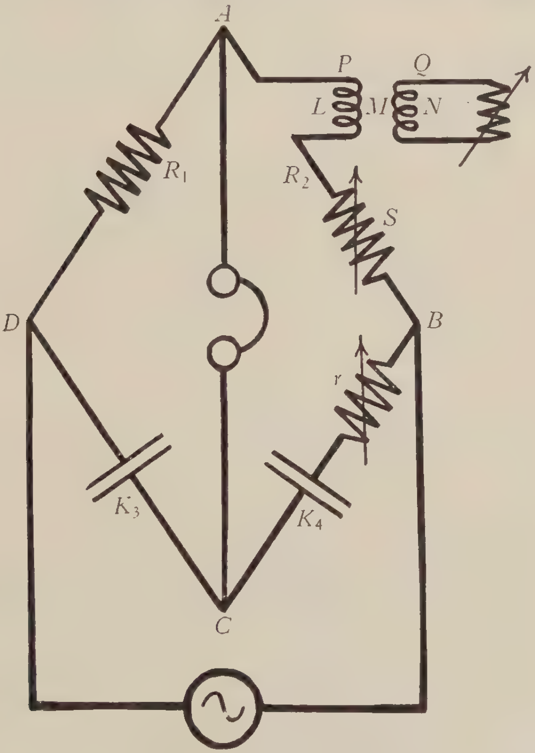

Figure 1. Theoretical circuit.

§ 3. EXPERIMENTAL PROCEDURE

To investigate the method experimentally the circuit shown in figure 2 was used, being the arrangement shown in figure 1 with a Wagner earth system added to eliminate earth-capacity effects. The resistance R_1 was a non-inductive resistance of 500 Ω.; K_3 and K_4 were standard mica condensers of 0·2 μF., both of the same type; and the inductances L and N were two coils of about 500 turns each, with a mean diameter of about 20 cm. S, s, and r were non-inductive resistances from boxes capable of adjustment to 0·1 Ω. A fractional-ohm box reading to 0·01 Ω. was also included in the arm AB. A resistance box in series with the secondary was capable of adjustment in steps of 1 Ω. As a detector, high-resistance telephones were used, alone or in conjunction with a step-up transformer whose impedance matched that of the bridge.

The source of alternating current was an audio-frequency valve oscillator with a variable condenser in the grid circuit. The frequency was first set to that of one of a series of tuning-forks held near the telephone head-bands, and was maintained constant by the aid of a variable condenser of 0·0005 μF. in parallel with the main grid condenser, the capacity being adjusted until coincidence of the two frequencies, as shown by the absence of beats, was attained. The double balances at frequencies of 2048, 1024, 768, 640, 512 and 428 c. sec. were found, and the graph, figure 3, shows the observed values of $(S_0 - S)_{\mathrm{max.}}$ plotted against frequency.

Since the ear is better able to discern the equality of two sounds of faint intensity than to find directly the point of complete silence of the fundamental in the presence of its harmonics, the procedure followed was to place in the R_2 arm a decade dial-box containing a set of 0·1-Ω. coils, and in series with it a 0·1-Ω. box subdivided to 0·01 Ω. The null point having been approximated to as closely as possible by a setting of the 0·01-Ω. dial, the 0·1-Ω. dial is changed alternately by 0·1 Ω. on either side. The correct null point is that for which the same sound-intensity occurs for each of the alternate settings. In this way accuracy to 0·01 Ω. in R_2 can be secured.

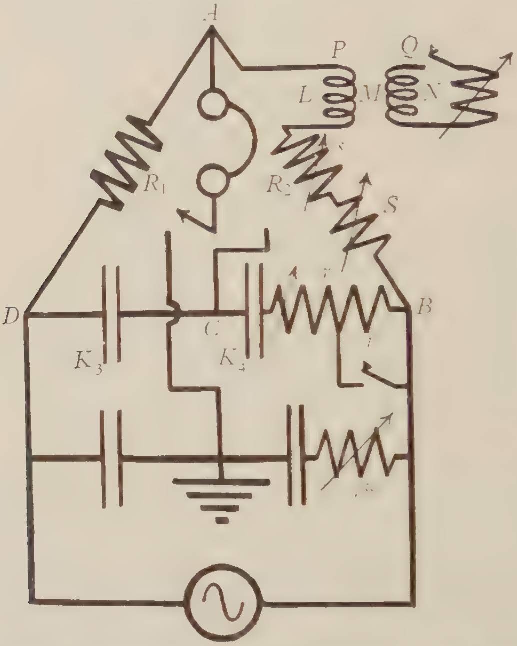

Figure 2. Experimental arrangement showing bridge with Wagner earthing arrangement. Resistance $R_2 = P + s + S$.

§ 4. CORRECTIONS DUE TO RESIDUALS

Variations from a linear relationship between $(P' - P)_{\mathrm{max.}}$ and frequency may arise from impurity of M, and from variation of N with frequency. It has been shown* that the phase-defect δ of induced e.m.f. in the secondary of an impure mutual inductance is given by δ

$$\delta = \tan^{-1} \sigma / pM,$$

where σ has the dimensions of a resistance and measures the impurity of the mutual inductance.

Thus $$e_s = (\sigma + jpM) i_p,$$

where e_s is the induced e.m.f. in the secondary and i_p the current in the primary at the same instant. e_s, i_p

By applying this to the fundamental formulae we can show that the effective resistance and inductance of the primary can be represented by the expressions

$$P' = P + (p^2M^2Q - 2p^2M\sigma N)/(Q^2 + p^2N^2)$$
$$L' = L - (p^2M^2N + 2M\sigma Q)/(Q^2 + p^2N^2).$$

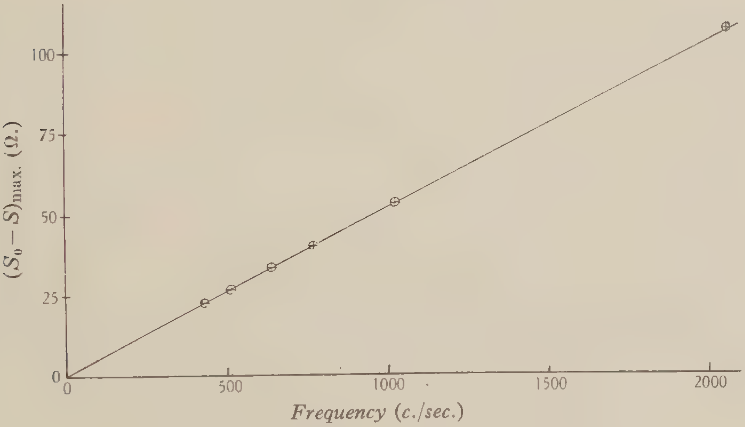

Figure 3. Variation of $(S_0 - S)_{\text{max.}}$ with frequency.

When the condition $Q = pN$ is fulfilled these equations reduce to

$$P' = P + pM^2/2N - M\sigma/N,$$
$$L' = L - M^2/2N - M\sigma/pN.$$

The effective value of P' now includes a small term independent of the frequency and the effective inductance a small term proportional to σ and inversely proportional to the frequency.

Over the audio-frequency range the change in the effective self-inductance of a coil due to change in frequency is limited to the effect of self-capacity which, in a large coil, may be quite appreciable. Regarding the distributed self-capacitance of a coil as equivalent to a small condenser of fixed value in parallel with it, we may write the vector impedance z of the coil z

$$z = [R + jp\{L(1 - p^2CL) - CR^2\}]/\{(1 - p^2CL)^2 + p^2C^2R^2\}.$$

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* *Proc. Phys. Soc.* **33**, 312 (1921).

L' The effective inductance L' will be given by

$$L' \fallingdotseq L/(1 - p^2CL),$$

R' and the effective resistance R' by

$$R' \fallingdotseq R/(1 - 2p^2CL),$$

terms involving higher powers of C being neglected.

Since $k = N/\pi M^2$ in the expression 4 (*a*), a change in the value of N due to frequency may cause the observed values of $(P' - P)_{\text{max.}}$ to depart slightly from strict linearity at high frequencies. Hence it is necessary to keep the self-capacitance of the secondary as low as possible, in which case the natural frequency of the coil will be much higher than the frequency under measurement.

§ 5. FREQUENCY-DETERMINATION

At the outset of a determination of the frequency of any source of supply the secondary is on open circuit, and the bridge is already balanced at known settings of the resistances in arms AB and BC, apart from a slight completing adjustment in the AB arm which depends on the temperature of the room. This adjustment is now made in s, and r is altered by the predetermined value r'. The secondary circuit is closed, and S and Q are now varied in conjunction until the balance is restored. The new reading of S is noted, and hence $(S_0 - S)_{\text{max.}}$ is found. The frequency is determined to a close approximation from the relation

$$f = k\,(S_0 - S)_{\text{max.}}$$

The small correction term arising from the effects discussed above is read off from a correction chart, and is added to produce the final value.

§ 6. SOME PRACTICAL CONSIDERATIONS

As is indicated in figure 3, very good correspondence with the linear law is found for frequencies up to about 1500, after which the curve rises above the straight line. This, as has been shown, is due to the variation of N with frequency, and can be reduced by making the self-inductance of the secondary coil smaller than that of the primary and by winding it in such a way as to keep the self-capacity low.

In designing an instrument embodying the method here described, the quantity $(r - r')$ could be short-circuited in the K_1 arm by means of the same switching arrangement as that which closes the secondary circuit.

Since both Q and the maximum change in S are proportional to the frequency, a single control can be provided for varying both resistances together, an auxiliary control consisting of a small rheostat being included in the arm AB to set the instrument for zero and to allow for slight changes in the resistance of the coil due to temperature fluctuations. A small rheostat can similarly be included in the arm BC to compensate for the slight variation of L with frequency.

Since k in the expression 4 (*a*) has the value $N/\pi M^2$, a decrease of N and an increase of M will make the observed value of $(P' - P)_{\max.}$ larger. Thus the value of M has to be made as large as possible, and this sets a limit to the reduction of N.

Figure 4 is a typical illustration of the accuracy with which the maximum setting of $(S_0 - S)$ can be approached, and shows the variation of this quantity with Q for a frequency of 768 c./sec.

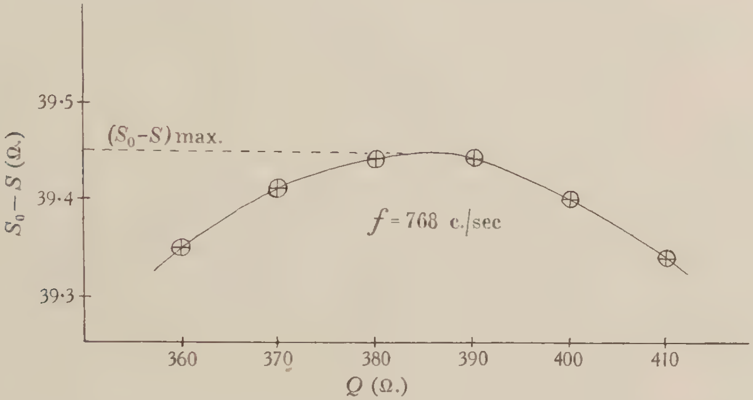

Figure 4. Variation of $(S_0 - S)$ with Q at a constant frequency of 768 c./sec.

§ 7. ACKNOWLEDGMENTS

This work was carried out in the Physics Research Laboratory of the Sir John Cass Technical Institute, London. My best thanks are due to Dr D. Owen for his advice and encouragement.

535·338·4 : 546·19

THE BAND SPECTRUM OF ARSENIC OXIDE (AsO)

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Received May 17, 1934.

ABSTRACT. Two systems of bands have been photographed under moderately high dispersion, and their vibrational structure has been analysed. The *A* system degrades towards the red and extends from λ 3450 to λ 2950, and the *B* system degrades away from the red and extends from λ 2800 to λ 2350. Both are doublet systems, and each component band has a double head formed by two branches. The systems arise from transitions between two excited $^2\Sigma$ levels and a $^2\Pi$ ground level having a separation of 1026 cm.$^{-1}$ between the Π components.

§ 1. INTRODUCTORY

The spectrum of arsenic oxide, so far as the author is aware, has not previously been described. His attention was directed to it by Dr R. W. B. Pearse, of the Imperial College of Science, who noted it on some plates which had been taken in a search for the spectrum of arsenic hydride. The oxide spectrum includes two systems of bands which, for convenience of reference, have been designated *A* and *B* in what follows. The *A* system consists of bands which are degraded towards the red and extend from λ 3450 to λ 2950, whilst the bands of the *B* system are degraded away from the red and occupy the region λ 2800 to λ 2350.

The vibrational analysis of the spectrum has shown that the bands originate in a diatomic molecule, and in view of the experimental conditions necessary for their production it must be concluded that the molecule is AsO. The ground level has been found to be of $^2\Pi$ type with a wide separation, and the *A* and *B* systems of bands are respectively produced by transitions from two higher levels of $^2\Sigma$ type.

§ 2. LIGHT-SOURCES EMPLOYED

The first source used to obtain the spectrum was a high-tension alternating-current arc between pieces of metallic arsenic held in suitable holders 5 mm. apart. The axis of the arc was horizontal and the current was taken from a transformer supplying about 0·2 A. at 10,000 V. Owing to the electrical instability of the arc, a stabilizing or ballast resistance was necessary. This had a maximum resistance of 25 Ω. and was connected in series with the primary winding of the transformer. The secondary current could be adjusted to a suitable value by means of this rheostat. After the arc had been running for several minutes the arsenic would catch fire, burning with a white flame and giving off clouds of oxide fumes which had to be carried into the flues by a fan. When once set alight the arsenic would, under suitable conditions, continue to burn, and the high-tension arc thus served to brighten the flame in a manner similar to that employed in producing the spectrum of tin oxide*. The temperature of this source was comparatively low and the bands were correspondingly short, so that the weaker heads were more clearly displayed than in hotter sources.

The loose crystalline structure of the arsenic made it difficult to grip the irregular lumps satisfactorily, and also frequently caused them to fall to pieces when partly consumed in the arc. A modification was therefore introduced by which small pieces or powder could be used. The arc was arranged vertically, the lower pole being an iron cup of internal diameter 2·5 cm., holding the coarse arsenic powder, whilst the upper pole was a stout copper rod cooled by a stream of running water, figure 1. The cooling of the copper in this way prevented excessive radiation of copper lines, as a result, no doubt, of the film of arsenic compounds which condensed over the copper surface.

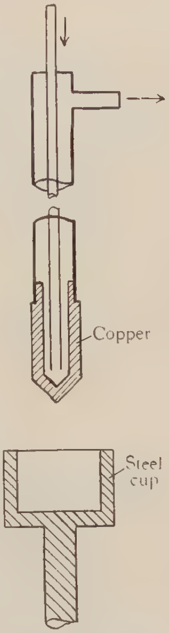

Figure 1. Water-cooled pole for high-tension arc.

A discharge tube of the usual H type has also been used to obtain the AsO bands. The tube was made of pyrex with quartz windows and aluminium electrodes. A side pocket near the capillary was filled with arsenic oxide powder, As_2O_3, and the ground stopper was fitted into place. Owing to the high temperature at which it was necessary to run the tube the ground seal could not be treated with tap grease, and a thin film of vacuum wax was melted into the groove above the stopper. After the air had been exhausted a discharge from a transformer was passed through the tube and the oxide pocket was heated sufficiently to vaporize the substance.

A third source of the spectrum was the carbon arc. The lower carbon was 18 mm. in diameter and drilled in the centre with an 8-mm. hole about 1 cm. deep. The coarse powder was packed into this cavity and the arc was struck between it and the upper 6-mm. carbon. The arc could be drawn out into a flame several centimetres long, and this was found to be the best condition for the production of the oxide spectrum. When the image of the centre of the arc was focused on the slit the *B* system of bands appeared in absorption. This apparently occurred as a result of absorption in the outer cool flame surrounding the white hot inner core of the arc, which emits a strong continuous radiation. This carbon-arc source was found useful in providing a simple method of obtaining the absorption spectrum, but it had definite disadvantages for the *A* system on account of the presence of CN bands.

The effect of temperature on the relative intensities of lines of a band has been discussed by Jevons†, and the advantages of a low-temperature source for rotational analysis has been pointed out; in the vibrational analysis also such a source is preferable to one at a high temperature. Each band is then less extensive and consequently the tails of the stronger bands do not mask the weaker heads. Of the three sources described above—high-tension arc, discharge tube and carbon arc—the shortest bands were found with the discharge tube, which yields heads that appear as little more than lines. The bands in the high-tension arc also, however, are short and have been found the most suitable for measurements, whilst the self-absorption obtained in the arc has given useful confirmation of the analysis.

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* F. C. Connelly, *Proc. Phys. Soc.* 42, 28 (1933).

† W. Jevons, *Report on Spectra of Diatomic Molecules*, p. 45 (Phys. Soc. 1932).

§ 3. DETERMINATION OF WAVE-LENGTHS

Photographs of the three sources have been obtained with Hilger quartz spectrographs E 2 and E 1; and in addition the *A* system of bands was photographed in the first order of the 10-ft. concave grating of this laboratory. The average dispersions of the three instruments in the two regions occupied by the AsO bands are as shown in table 1.

Table 1

Spectrograph	Dispersion (Å./mm.)	
	Region *A*	Region *B*
E 2	20	9·2
E 1	6	2·8
Grating	5·4	—

Imperial Ordinary plates (H and D 150) were used, and good photographs of the high-tension arc were obtained on the E 1 spectrograph with exposures of 20 minutes. The iron arc was used as a source of reference spectra. The photographs were measured in the usual manner with a Hilger photo-measuring micrometer. The wave-lengths of the iron lines used as standards for interpolation were, as far as possible, taken from the list published by the International Astronomical Union*. These were supplemented in the region of the *B* system with vacuum-arc wave-lengths given by Burns and Walters†. Wave-lengths of all the band-heads measured are shown in tables 2 and 3, which also indicate the type of head, the v', v'' values allotted in the analysis, the wave-numbers *in vacuo*, and the estimated intensities of the bands.

§ 4. THE *A* SYSTEM

Description of the bands. The system has a wide doublet structure in which the separation is greater than the vibrational spacing, so that its doublet character is not immediately evident. The more refrangible and the less refrangible components are indicated in the plate at (1) and in the tables and diagrams by letters (*a*) and (*b*) respectively. Thus the *a* (0, 0) is the very strong band at λ 3172·40 (ν = 31512·8) and the sequences *a* (0, 0), *a* (1, 1), *a* (2, 2)—*a* (1, 0), *a* (2, 1), *a* (3, 2)—*a* (2, 0), *a* (3, 1), *a* (4, 2) form prominent features of the system. Each of these bands has itself two close heads, the separation of which varies progressively from band to band. These heads have been attributed to *R* and *Q* branches.

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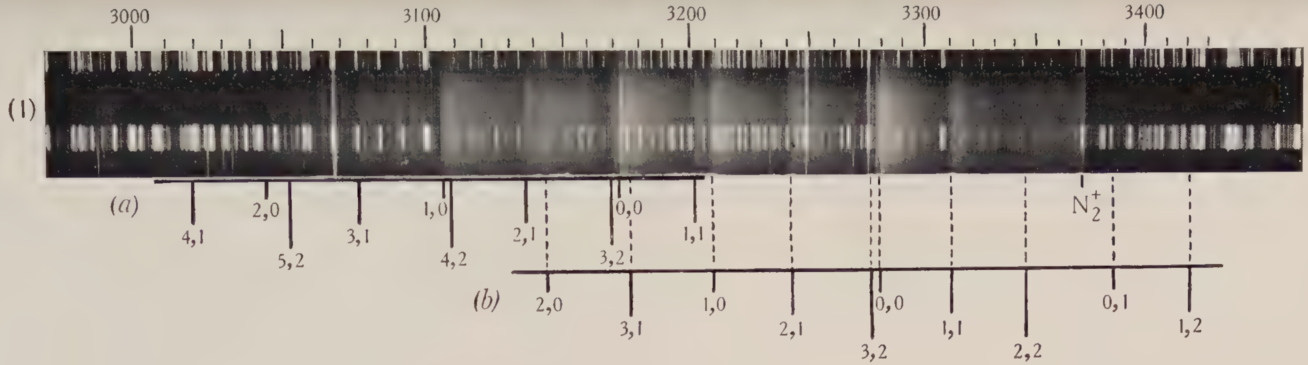
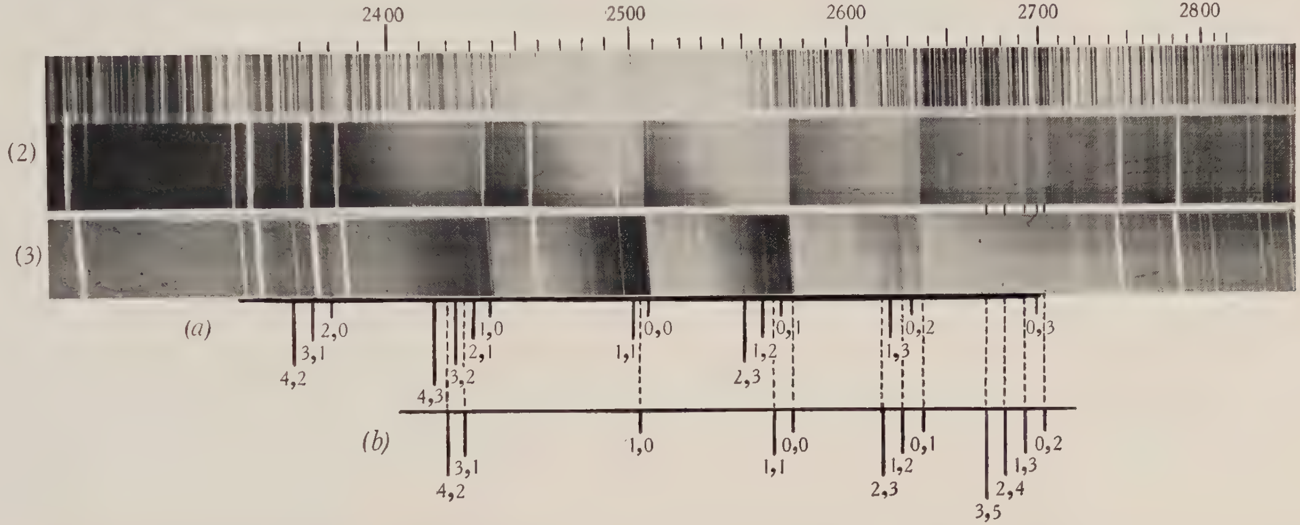
* *Trans. I.A.U.* **4**, 70 (1932).

† *Publ. Allegh. Obs.* **8**, No. 4 (1931).

A System



B System



(1) The *A* system photographed in the high-tension arc with the Hilger E 1 quartz spectrograph. The close double heads of each band are due to *R* and *Q* branches. The *Q* heads of the principal bands are indicated by lines below the spectrum, and the doublet structure is clearly shown by the sequences of (*a*) and (*b*) components.

(2) The *B* system produced in the high-tension arc and photographed with the E 2 instrument. The (*a*) and (*b*) components have been indicated as before. The vibrational spacings of the initial and final levels are nearly equal, causing close sequences, and further crowding together is due to the similarity of the doublet spacing.

(3) The *B* system self-absorbed in the carbon arc. Only those bands having low values of v'' appear with appreciable strength.

Table 2. *A* system (degraded to the red)

λ in air, and intensity	ν *in vacuo*	v', v''	Type of head
3417·83 (1)	29250·0	*b* (1, 2)	*Q*
3415·85 (1)	29266·9	*b* (1, 2)	*R*
3385·22 (1)	29531·7	*b* (0, 1)	*Q*
3382·90 (1)	29552·0	*b* (0, 1)	*R*
3343·80 (1)	29897·0	*b* (2, 2)	*Q*
3310·71 (4)	30196·3	*b* (1, 1)	*Q*
3309·25 (2)	30210·6	*b* (1, 1)	*R*
3279·15 (9)	30486·9	*b* (0, 0)	*Q*
3277·21 (8)	30504·9	*b* (0, 0)	*R*
3275·38 (2)	30522·1	*b* (3, 2)	*Q*
3241·44 (4)	30841·6	*b* (2, 1)	*Q*
3240·11 (3)	30854·3	*b* (2, 1)	*R*
3209·13 (6)	31152·1	*b* (1, 0)	*Q*
3207·76 (4)	31165·4	*b* (1, 0)	*R*
3202·05 (4)	31221·0	*a* (1, 1)	*Q*
3200·16 (2)	31239·4	*a* (1, 1)	*R*
3177·60 (3)	31461·0	*b* (3, 1)	*Q*
3172·40 (8)	31512·8	*a* (0, 0)	*Q*
3170·62 (5)	31530·4	*a* (0, 0)	*R*
3169·13 (2)	31545·3	*a* (3, 2)	*Q*
3151·16 (1)	31725·2	*b* (5, 2)	*Q*
3150·03 (1)	31736·6	*b* (5, 2)	*R*
3144·14 (4)	31796·0	*b* (2, 0)	*Q*
3143·07 (2)	31806·8	*b* (2, 0)	*R*
3137·23 (4)	31866·0	*a* (2, 1)	*Q*
3135·59 (4)	31882·7	*a* (2, 1)	*R*
3123·32 (1)	32080·0	*b* (4, 1)	*Q*
3106·83 (6)	32177·8	*a* (1, 0)	*Q*
3105·64 (4)	32189·9	*a* (1, 0)	*R*
3075·80 (2)	32502·0	*a* (3, 1)	*Q*
3052·14 (1)	32754·4	*a* (5, 2)	*Q*
3051·50 (0)	32761·3	*a* (5, 2)	*R*
3045·85 (2)	32822·0	*a* (2, 0)	*Q*
3044·72 (1)	32834·2	*a* (2, 0)	*R*
3019·28 (1)	33110·8	*a* (4, 1)	*Q*

The (*b*) components also form well-marked sequences with spacings practically identical with those between the bands of the (*a*) sequences. Each band, however, is displaced towards the red with respect to the corresponding (*a*) component by approximately 1026 wave-numbers; e.g. the *b* (0, 0) band is at λ 3279·15 (ν = 30486·9). Again, each band has an *R* and *Q* head, the separation between them changing in magnitude from band to band in the same direction as in the corresponding (*a*) components. The system may therefore be considered to be made up of two sets of bands, the arrangement in one set being identical with that in the other but such that the bands in the first set are displaced from the second by 1026 wave-numbers.

Vibrational analysis. Table 4 shows the arrangement of the *Q* heads in a Deslandres scheme; the (*a*) and (*b*) components of each band are arranged for convenience in pairs one below the other. As the *Q* heads are very close to the origins, it may be considered that these values also represent the positions of the origins of the bands within the limits of experimental error. The next step is to derive an equation to represent all the *Q* heads by giving appropriate values to

Table 3. *B* system (degraded away from red)

λ in air, and intensity	ν *in vacuo*	v', v''	Type of head
2772·80 (0)	36054·0	*b* (0, 3)	*P*
2771·80 (1)	36066·0	*b* (0, 3)	*Q*
2759·90 (0)	36222·0	*b* (1, 4)	*P*
2759·00 (1)	36234·0	*b* (1, 4)	*Q*
2747·05 (0)	36392·0	*b* (2, 5)	*Q*
2702·63 (2)	36990·0	*b* (0, 2)	*P*
2701·75 (3)	37002·1	*b* (0, 2)	*Q*
2695·37 (0)	37089·7	*a* (0, 3)	*Q*
2691·71 (2)	37140·1	*b* (1, 3)	*P*
2690·79 (3)	37152·8	*b* (1, 3)	*Q*
2683·40 (0)	37256·0	*a* (1, 4)	*Q*
2680·87 (1)	37290·3	*b* (2, 4)	*P*
2680·01 (2)	37302·2	*b* (2, 4)	*Q*
2673·57 (0)	37392·0	*a* (2, 5)	*P*
2672·15 (0)	37412·0	*a* (2, 5)	*Q*
2670·54 (1)	37434·5	*b* (3, 5)	*P*
2669·37 (1)	37450·8	*b* (3, 5)	*Q*
2635·48 (4)	37932·5	*b* (0, 1)	*P*
2634·45 (5)	37947·3	*b* (0, 1)	*Q*
2629·96 (1)	38012·1	*a* (0, 2)	*P*
2629·12 (2)	38024·2	*a* (0, 2)	*Q*
2625·81 (2)	38072·1	*b* (1, 2)	*P*
2624·67 (4)	38088·6	*b* (1, 2)	*Q*
2619·57 (1)	38162·8	*a* (1, 3)	*P*
2618·62 (1)	38177·0	*a* (1, 3)	*Q*
2617·46 (1)	38193·6	*b* (2, 3)	*P*
2615·75 (1)	38218·6	*b* (2, 3)	*Q*
2570·87 (6)	38885·7	*b* (0, 0)	*P*
2569·67 (8)	38903·9	*b* (0, 0)	*Q*
2566·24 (3)	38955·9	*a* (0, 1)	*P*
2565·17 (4)	38972·1	*a* (0, 1)	*Q*
2562·30 (1)	39015·7	*b* (1, 1)	*P*
2561·21 (2)	39032·3	*b* (1, 1)	*Q*
2557·07 (3)	39095·6	*a* (1, 2)	*P*
2555·98 (3)	39112·2	*a* (1, 2)	*Q*
2552·80 (1)	39161·0	*b* (2, 2)	*Q*
2548·04 (1)	39234·1	*a* (2, 3)	*P*
2546·99 (1)	39250·3	*a* (2, 3)	*Q*
2538·20 (0)	39386·0	*a* (3, 4)	*Q*
2504·69 (6)	39913·1	*a* (0, 0)	*P*
2503·64 (7)	39929·8	*a* (0, 0)	*Q*
2501·03 (2)	39971·5	*b* (1, 0)	*P*
2499·94 (2)	39988·9	*b* (1, 0)	*Q*
2496·75 (1)	40040·0	*a* (1, 1)	*P*
2495·60 (2)	40058·5	*a* (1, 1)	*Q*
2493·75 (1)	40088·1	*b* (2, 1)	*P*
2492·62 (1)	40106·3	*b* (2, 1)	*Q*
2488·79 (0)	40168·0	*a* (2, 2)	*P*
2487·70 (0)	40185·6	*a* (2, 2)	*Q*
2486·36 (1)	40207·3	*b* (3, 2)	*P*
2485·37 (1)	40223·1	*b* (3, 2)	*Q*
2438·49 (3)	40996·5	*a* (1, 0)	*P*
2437·33 (4)	41016·1	*a* (1, 0)	*Q*
2435·63 (0)	41044·6	*b* (2, 0)	*P*
2434·66 (1)	41061·0	*b* (2, 0)	*Q*
2431·52 (1)	41114·1	*a* (2, 1)	*P*
2430·41 (2)	41132·8	*a* (2, 1)	*Q*
2428·10 (1)	41172·0	*b* (3, 1)	*Q*
2424·72 (1)	41229·3	*a* (3, 2)	*P*
2423·59 (2)	41248·6	*a* (3, 2)	*Q*
2417·20 (1)	41357·0	*a* (4, 3)	*Q*
2376·30 (2)	42069·3	*a* (2, 0)	*P*
2375·08 (2)	42090·9	*a* (2, 0)	*Q*
2370·35 (0)	42174·9	*a* (3, 1)	*P*
2369·28 (1)	42194·1	*a* (3, 1)	*Q*
2363·35 (0)	42299·0	*a* (4, 2)	*Q*

Table 4. *A* system. *Q* heads

v' \ v''		0		1		2	²Π
0	*a*	31512·8	—	—	—	—	
	b	30486·9	955·2	29531·7	—	—	
	Δ*a*	665·0		—			
	Δ*b*	665·2		664·6			
1	*a*	32177·8	956·8	31221·0	—	—	
	b	31152·1	955·8	30196·3	946·3	29250·0	
	Δ*a*	644·0		645·0		—	
	Δ*b*	643·9		645·3		647·0	
2	*a*	32822·0	956·0	31866·0	944·0	30922·0	
	b	31796·0	954·4	30841·6	945·0	29897·0	
	Δ*a*			636·0		623·0	
	Δ*b*			620·0		625·0	
3	*a*			32502·0	947·0	31545·3	
	b			31461·0	939·0	30522·1	
	Δ*a*			609·0			
	Δ*b*			619·0			
4	*a*	—		33110·8		—	
	b	—		32080·0		—	
5	*a*	—		—		32754·4	
	b	—				31725·2	
²Σ							

v' and v''. In the manner indicated by W. Jevons* the following equations have been independently derived from the (*a*) and (*b*) components:

For the *Q* heads denoted by (*a*)

$$\nu = 31655{\cdot}4 + [685{\cdot}6\,(v'+\tfrac{1}{2}) - 10{\cdot}3\,(v'+\tfrac{1}{2})^2] - [967{\cdot}8\,(v''+\tfrac{1}{2}) - 5{\cdot}7\,(v''+\tfrac{1}{2})^2];$$

For the *Q* heads denoted by (*b*)

$$\nu = 30628{\cdot}6 + [685{\cdot}2\,(v'+\tfrac{1}{2}) - 10{\cdot}2\,(v'+\tfrac{1}{2})^2] - [966{\cdot}3\,(v''+\tfrac{1}{2}) - 5{\cdot}6\,(v''+\tfrac{1}{2})^2].$$

These formulae represent the observed band-heads closely, as will be seen from the values of observed and computed wave-numbers in table 5.

Table 5. Observed and computed wave-numbers

v' \ v''		0	1	2
0	*a*	− 0·3	—	—
	b	+ 0·6	+ 0·5	—
1	*a*	+ 0·7	− 0·7	—
	b	+ 1·0	+ 0·3	− 2·1
2	*a*	− 1·5	− 0·1	+ 0·9
	b	− 0·5	+ 0·2	− 0·5
3	*a*	—	+ 1·2	+ 0·4
	b	—	− 3·4	+ 1·6

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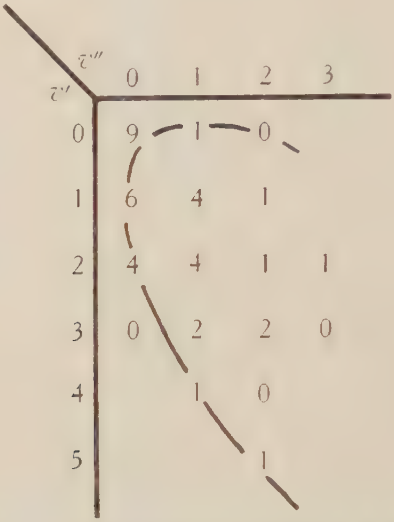
* *Report on Band Spectra of Diatomic Molecules*, p. 60 (Phys. Soc. 1933).

The estimated relative intensities of the various bands given in the wave-lengths table are shown by the conventional method in figure 2. The values of ω_e' and ω_e'' differ considerably, so that the Franck-Condon theory would predict a relatively wide Condon parabola. It will be seen that the curve for this system bears out the general theory so far as the limited number of bands permits.



v' \ v''	0	1	2	3
0	9	1	0	
1	6	4	1	
2	4	4	1	1
3	0	2	2	0
4		1	0	
5			1	

Figure 2. Relative intensities of bands in *A* system.

§ 5. THE *B* SYSTEM

Description of bands. The *B* system is illustrated in the plate at (2) and (3). It consists of five or six groups within which the bands are crowded together, with intermediate spaces almost free of bands. As in the *A* system there are close double heads, but they degrade away from the red; they are apparently *P* and *Q* heads, since the spacing varies in different bands. The confusion of the bands results from the approximate equality of three separations, namely the two vibrational spacings and the doublet spacing of the lower electronic level. This latter spacing is the same as in the *A* system (1026 wave-numbers), so that here again two components, denoted by (*a*) and (*b*), are found for each value of v' and v''. The *a* (0, 0) and *b* (0, 0) bands are at λ 2503·64 ($\nu = 39929·8$) and λ 2570·87 ($\nu = 38903·9$) and the (*a*) and (*b*) components of each of the principal bands are indicated in the plate.

In this system also the bands may be divided into two parts: the arrangement of the (*a*) bands is the same as that of the (*b*) bands, but each of the (*a*) components is 1026 wave-numbers further from the red than the corresponding (*b*) component. The similarity is not so easy to see as in the other system owing to the overlapping, but the vibrational-analysis scheme shows the doublet nature quite definitely.

Vibrational analysis. Details of the band-heads of the *B* system are included in table 3. The *Q* heads are shown arranged in a Deslandres scheme in table 6. As before, the two components (*a*) and (*b*) are bracketed together.

Table 6. *B* system. *Q* heads

v''		0	1	2	3	4	5
0	*a*	39929·8 *957·7*	38972·1 *947·9*	38024·2 *934·5*	37089·7	—	—
	b	38903·9 *956·6*	37947·3 *945·2*	37002·1 *936·0*	36066·0	—	—
		1086·3	*1086·4*	*1088·0*	*1087·3*		
		1086·0	*1085·0*	*1086·5*	*1087·0*		
1	*a*	41016·1 *957·6*	40058·5 *946·3*	39112·2 *935·2*	38177·0 *921·0*	37256·0	—
	b	39988·9 *956·6*	39032·3 *943·7*	38088·6 *935·8*	37152·8 *919·0*	36234·0	—
		1074·8	*1074·3*	*1073·4*	*1073·3*	—	
		1072·0	*1074·0*	*1072·0*	*1065·8*	*1068·0*	
2	*a*	42090·9 *958·1*	41132·8 *947·2*	40185·6 *935·3*	39250·3	—	37412·0
	b	41061·9 *955·6*	40106·3 *945·0*	39161·0 *942·0*	38218·6 *916·4*	37302·2 *910·0*	36392·0
			1061·3	*1063·0*			*1059·0*
			1063·7	*1062·0*			—
3	*a*	—	42194·1 *945·5*	41248·6	—	—	—
	b	—	41170·0 *946·9*	40223·1	—	—	37450·8
				1051·0			
				—			
4	*a*	—	—	42299·0 *942·0*	—	—	—
	b	—	—	—	—	—	—

The formulae for the *Q* heads are derived by the method previously mentioned in connexion with the *A* system, and are as follows:

For the (*a*) components

$$\nu = 39865{\cdot}7 + [1099{\cdot}0\,(v' + \tfrac{1}{2}) - 6{\cdot}2\,(v' + \tfrac{1}{2})^2] - [970{\cdot}0\,(v'' + \tfrac{1}{2}) - 5{\cdot}8\,(v'' + \tfrac{1}{2})^2];$$

For the (*b*) components

$$\nu = 38839{\cdot}2 + [1097{\cdot}6\,(v' + \tfrac{1}{2}) - 6{\cdot}0\,(v' + \tfrac{1}{2})^2] - [968{\cdot}2\,(v'' + \tfrac{1}{2}) - 5{\cdot}7\,(v'' + \tfrac{1}{2})^2].$$

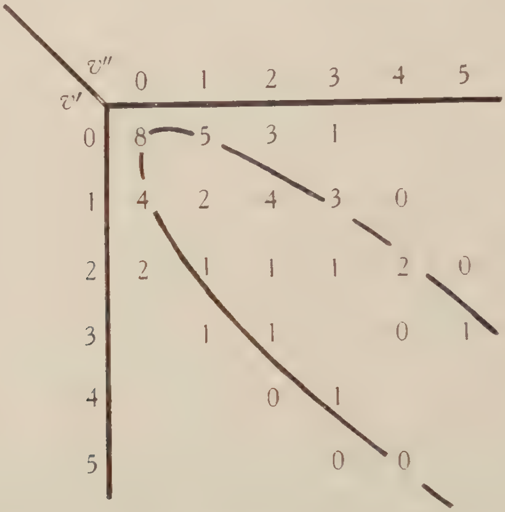
The separations between corresponding *P* and *Q* heads are shown in table 7. In spite of random variations due to errors in measurement, it will be seen that there is a definite tendency for the intervals to increase as v' increases and to decrease as v'' increases. For practical purposes these intervals are the distances between *P* heads and the origins, and such changes are to be expected from the theory of the rotational structure of bands.

Table 7. *B* system. Interval (*Q* head–*P* head)

		0	1	2	3	4	5
0	*a*	16·7	16·2	12·1	—	—	—
	b	18·2	14·8	12·1	12·0	—	—
1	*a*	19·6	18·5	16·6	14·2	—	—
	b	17·4	16·6	16·5	12·7	12·0	—
2	*a*	21·6	18·7	17·6	16·2	—	20·0
	b	16·4	18·2	—	25·0	11·9	—
3	*a*	—	19·2	19·3	—	—	—
	b	—	—	15·8	—	—	16·3

The estimated relative intensities of the *B* bands are indicated by numbers in figure 3. The Condon parabola of maximum intensities is here quite narrow, and this is in agreement with the Franck-Condon principle, which predicts such a curve when the vibrational constants are nearly equal in the initial and final electronic states.

The absorption spectrum. The spectrum obtained by self-absorption of the *B* system in the carbon arc is shown in the plate at (3). The relative intensities of the bands completely confirm the arrangement of the vibrational scheme. Only those having low values of v'' ought to be present; in fact only the bands for which $v'' = 0$ should appear strongly, even in a vapour at a moderately high temperature. Examination of the spectrum shows in a striking manner the high intensities of the two (0, 0), (1, 0) and (2, 0) bands relative to the (0, 1) bands which appear with relatively low intensity—compare the emission spectrum at (2)—and the (0, 2) bands which are not visible at all. The appearance of the system in absorption indicates that the lower electronic level involved in the transition must be the normal or ground state of the molecule, usually denoted by *X*.



v' v''	0	1	2	3	4	5
0	8	5	3	1		
1	4	2	4	3	0	
2	2	1	1	1	2	0
3		1	1		0	1
4			0	1		
5				0	0	

Figure 3. Relative intensities of bands in *B* system.

§ 6. CORRELATION OF THE TWO SYSTEMS

When we compare the data for the two systems, it is evident that the vibrational constants of the final levels are, within close limits, the same in both; it may therefore be concluded that the final electronic levels are equal. Furthermore, as the doublet spacing is also the same in both systems, this spacing must be that of a doublet final level. The wide spacing of this common lower level suggests a $^2\Pi$, and this is in accordance with the type assigned to the lower levels of similar systems in the spectra of NO and PO. In view of the ease with which the *B* system appears in absorption it may be taken that this $^2\Pi$ level is the ground state of the molecule.

The selection rules indicate that the upper levels also are expected to be of even multiplicity. The doublet spacing in the two systems is equal within the errors of measurement, so that the separations of the components of the upper levels must either be equal to each other (a very unlikely possibility) or both must be too small to be measurable. The appearance of strong Q branches shows that there must be changes in the type of level, i.e. the upper levels must be either Σ or Δ. It is very probable therefore that the levels are in each case $^2\Sigma$.

The electronic transitions concerned in the *A* and *B* systems are shown in figure 4.

The wide separation of 1026 wave-numbers between the two components of the $^2\Pi$ ground level is larger than that found in most of the molecules for which data are available. This is largely due to the fact that the spectra of very few molecules of high molecular weight have so far been examined. SnCl*, however, with 67 electrons has a $^2\Pi$ ground level with a spacing of 2360 wave-numbers, and HgH† with 81 electrons has 3684, whilst an excited $^2\Pi$ level of CdH‡ with 49 electrons has a separation of 1000 wave-numbers. The value of 1026 in the present case is therefore in accordance with the data for molecules of similar weight, and is not excessive.

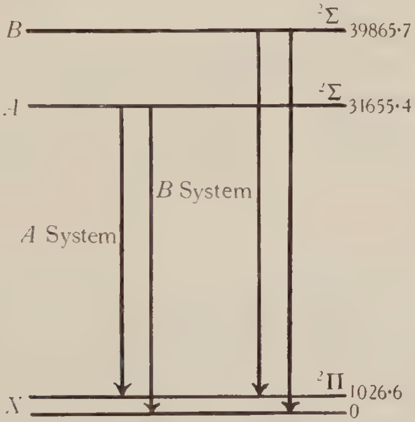


Figure 4. Electronic transitions in AsO.

§ 7. THE ENERGY OF DISSOCIATION

Values of D, the actual energy of dissociation from the lowest vibrational energy level ($v = 0$), can be obtained by the extrapolation method of Birge and Sponer§. Numerical values for the three states of the AsO molecule have thus been calculated to be

$B\ (^2\Sigma)$	6·09 V.
$A\ (^2\Sigma)$	1·32 V.
$X\ (^2\Pi)$	5·68 or 4·8 V., depending on which system formula is used.

* W. Jevons, *Proc. R.S.* **110**, 365 (1926).

† Hulthén, *Z. f. Phys.* **32**, 32 (1925).

‡ Svensson, *Z. f. Phys.* **50**, 333 (1930).

§ R. T. Birge and H. Sponer, *Phys. Rev.* **28**, 259 (1926).

§ 8. RELATED SPECTRA

Of the spectra of oxides of the other elements of the fifth group of the periodic table, only that of NO has been examined at all thoroughly. In this the ground level is $^2\Pi$ and two $^2\Sigma$ and a $^2\Pi$ excited levels are known also. The separation in the ground state is 121 wave-numbers. The γ and δ bands arise from transitions between the $^2\Sigma$ states and the $^2\Pi$ ground level, and have a very distinct doublet structure, each component having close *P* and *Q* heads. Although the γ bands are actually similar to the *B* system of AsO bands, the difference in $^2\Pi$ spacing has a great effect on the appearance of the spectrum.

Two systems of bands in the PO spectrum have been described by Petrikaln* and a vibrational analysis of one of these has since been given by Ghosh and Ball†. The transition classified in this case is from a $^2\Sigma$ excited level to a $^2\Pi$ ground state having a separation of 224 wave-numbers.

The molecule NS‡ has the same number of electrons as PO, namely 23, and it is interesting to note that the separation of the $^2\Pi$ ground level is 223 cm^{-1} There are in addition $^2\Sigma$ and $^2\Pi$ levels.

AsO with 41 electrons has, as described above, a $^2\Pi$ ground state with a separation of 1026 wave-numbers and two excited $^2\Sigma$ levels.

The remaining members of this sub-group, SbO and BiO, have been subjected to a preliminary examination, no fewer than four systems involving six levels having been proposed by Mukherji§ for SbO. The four systems are stated to be singlet ones and it appears that the vibrational constants of several of the levels are very nearly equal. Probably certain of the systems are in reality parts of a doublet system as in AsO but of even wider separation. From extrapolation, the spacing in the ground level may be expected to be of the order of 3000 wave-numbers, and such a doublet system would appear as two almost completely separated singlet ones. There is also an isotope of high relative abundance, and although the separation to be expected is rather small it may account for certain small differences in the vibrational constants of some of the levels.

A very similar arrangement of levels has been suggested for BiO by Ghosh‖. Four singlet systems arising from transitions between six different electronic levels have been proposed. These also may be a doublet system similar to that suggested for SbO.

These comparisons seem to confirm the classifications which have been suggested for AsO.

§ 9. ACKNOWLEDGMENTS

The author is indebted to Prof. A. Fowler, F.R.S. for much valuable advice in the preparation of this paper, and to Dr R. W. B. Pearse for bringing the spectrum to his notice and for subsequent suggestions.

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* *Z. f. Phys.* **51**, 395 (1928).
† *Z. f. Phys.* **71**, 362 (1931).
‡ Fowler and Bakker, *Proc. R.S.* **136**, 28 (1932).
§ *Z. f. Phys.* **70**, 552 (1931).
‖ *Z. f. Phys.* **86**, 241 (1933).

535.338.4 : 546.17

INTENSITY MEASUREMENTS IN THE FIRST POSITIVE BANDS OF NITROGEN

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Received May 31, 1934.

ABSTRACT. The integrated intensities of bands in the first positive system of nitrogen have been measured by the method of photographic photometry, the high-frequency discharge, the direct-current discharge and the afterglow of active nitrogen being used as sources. The measurements show that in the cases examined the probability of transition between two vibrational levels is independent of excitation conditions.

§ 1. INTRODUCTION

In several recent publications (1), (2), (3) it has been suggested that the probability of a transition between two energy-levels of a molecule depends upon the conditions of excitation. Further examination of this effect seemed desirable, and accordingly we have made measurements of the intensities of some of the bands of the first positive system of nitrogen. This system shows remarkable variations of intensity-distribution when different methods of excitation are used.

We have endeavoured to avoid several sources of error which may arise in photometric work of this kind.

§ 2. EXCITATION OF THE SPECTRUM

Active nitrogen. Commercial nitrogen from a cylinder was passed through a purification system consisting of tubes of phosphorus (to remove excess of oxygen), NaOH, $CaCl_2$ and P_2O_5. The gas was then led through a needle valve into the discharge tube, where it could be activated by a heavy condensed discharge. The resulting active nitrogen was led through a horizontal afterglow tube and was continuously pumped off as rapidly as possible by means of a Cenco Hyvac pump. The rate of the nitrogen supply was adjusted so as to give the maximum intensity of the afterglow in the horizontal tube. Light from this tube was condensed on to the slit of the spectrograph by means of a lens.

High-frequency discharge. Instead of activating the nitrogen by the condensed discharge, we fixed external electrodes to the horizontal tube and connected them to a high-frequency oscillator operating at about 10^7 c./sec. For the high-frequency discharge the gas pressure was maintained at about 0·1 mm. of mercury.

Direct current discharge. Electrodes sealed into the horizontal tube were connected to a 1500-volt direct-current generator in series with a 30,000-ohm resistance. The current was well smoothed by means of a 1-microfarad condenser across the generator terminals, to avoid the intermittence effect of which an account is given below. The pressure of the gas in this case was about 1 mm. of mercury.

§ 3. PHOTOMETRY

The photometric procedure employed was very similar to that used in measuring the intensities of the bands of boron monoxide(4). Since the active-nitrogen afterglow was very much weaker than the high-frequency or direct-current discharges the intensities of these latter were cut down with a neutral grey absorbing screen so that the same time of exposure could be used for all three modes of excitation. The exposure time for the standard lamp was also adjusted to the same value. Ilford hypersensitive panchromatic plates were found to be very suitable for the wave-length range required.

Since it was impossible to obtain with one exposure suitable densities for all the nitrogen bands, a composite absorbing screen was placed immediately in front of the spectrograph slit when these bands were being photographed. This screen consisted of three parts of different optical densities, each part covering approximately one third of the length of the slit. With this device, a single exposure gave three records of the nitrogen bands, of relative intensities about 100 : 46 : 19. The exact values of these relative intensities were determined from measurements of the peak densities of a band on each of the three spectra. With the aid of the (density, intensity) calibration curve for the plate at the appropriate wave-length the transmitted intensities were determined. It was necessary to make this determination separately for each of the three methods of excitation because of the difficulty of illuminating the length of the slit uniformly. The plate from which the final intensity-measurements were made gave the data for these determinations.

For the measurement of band-intensities, the automatic recording device described by Thompson(5) was used at first, but it proved to be less satisfactory here than in the measurements of the intensities of the BO bands(4). This was chiefly due to the imperfect separation of the nitrogen bands, in consequence of which there was no unexposed plate between the bands. The adjustment of the template was therefore rather difficult and uncertain.

The procedure finally adopted was to measure the densities within a band at a number of points, and to read off the corresponding intensities from the calibration curve. These intensities were then plotted against the position on the microphotometer record. For each band, the area under the resulting curve when corrected for dispersion, the energy function of the standard lamp(4), and the transmission of the screen was proportional to the integrated intensity of the band. A (density, intensity) calibration curve was required for each band.

This method, though more laborious, is greatly to be preferred to the estimation of band-intensities by measurement of the peak values only, on account of possible alterations in the intensity-distribution within a band when different modes of excitation are used.

§ 4. INTERMITTENCE EFFECT

In order to see whether the calibration curve which was obtained from exposures made with a continuous source, namely the standard lamp, could be used with the intermittent high-frequency discharge, the transmissions of the composite screen were measured by means of exposures made with these two sources. When corrections were made for a slight lack of uniformity in the illumination over the length of the spectrograph slit the results agreed to within 3 per cent. From this we infer that the intermittence effect is not appreciable with the high-frequency discharge. The effect of the discharge from the d.-c. generator was quite different, however, unless the discharge was smoothed. Examination with a cathode-ray oscillograph showed that the generator voltage was subject to large periodic fluctuations, and this apparently resulted in a lack of agreement between the screen transmissions measured when the standard lamp and the discharge tube respectively were used as sources. The difference was of the order of 7 per cent. When the generator voltage was smoothed, this difference disappeared.

§ 5. RESULTS

The final results of the measurements are given in the table. All the bands in the red, yellow and green sequences which were of sufficient intensity have been measured, with the exception of the 4–1 band at $\lambda = 6788$ Å. At this point the

Table. Intensities of bands in the first positive system of nitrogen

Band	Measured intensity			Intensity × correlation-factor	
	Active nitrogen	Direct-current discharge	High-frequency discharge	Active nitrogen	Direct-current discharge
5–1	—	38·6	16·8	—	15·8
5–2	—	402	154	—	164
6–2	—	76·5	33·3	—	31·6
6–3	—	453	177	—	187
7–3	—	62·3	36·7	—	36·3
7–4	—	209	120	—	122
8–4	—	58·2	30·0	—	31·2
8–5	—	118	66	—	63·3
9–4	—	9·2	5·02	—	4·90
9–5	—	57·1	30·0	—	31·0
9–6	—	74·0	39·1	—	39·5
10–5	—	10·4	4·61	—	4·87
10–6	12·8	62·0	29·4	30·6	29·1
10–7	9·9	52·1	24·5	23·7	24·4
11–6	10·2	12·6	6·80	6·24	6·85
11–7	52·0	55·3	30·0	31·8	30·1
11–8	27·0	28·9	15·9	16·5	15·7
12–7	5·90	9·15	7·45	7·50	7·14
12–8	19·0	32·7	24·4	24·1	25·5
12–9 4–0	5·55	20·9	15·1	7·1	16·3

change in plate sensitivity with wave-length becomes too rapid to allow of accurate intensity-measurements.

The intensities in the second, third and fourth columns differ on account of differing population of the upper levels, but it seems likely that the probability of transition between levels should be independent of excitation conditions. If this is true, the intensities of any band when excited by the three different methods should be proportional to the populations of the upper states in the three cases, and the proportionality factors should be constant for all bands having a common upper vibrational level.

This seems to be the case. The mean values of these factors have been found for each upper level, and by means of these the intensities of bands in the direct-current discharge and in the afterglow have been adjusted to the values which they would have had if the population of the upper levels had been the same as the population of these levels in the high-frequency discharge. The fifth and sixth columns of the table give the results of this adjustment, and it will be noticed that the agreement with the values in the fourth column is in most cases very close. The only marked deviation occurs in the 12–9 band, but this can be explained by the superposition of the 4–0 band, which is of appreciable intensity in the high-frequency and direct-current discharges, but is very weak in the afterglow(6).

On the basis of the whole of the results it may be concluded that the transition-probabilities in the three modes of excitation agree to within about 3 per cent, the maximum individual deviation being 7 per cent. We attribute these small deviations to experimental error, due chiefly to imperfect separation of the bands.

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ON THE AUTOMATIC REGISTRATION OF THE AMPLITUDE OF DOWNCOMING WIRELESS WAVES

Part I

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Communicated by Prof. E. V. Appleton, F.R.S., May 25, 1934.

ABSTRACT. An adaptation of the Breit and Tuve method of echo delineation, by means of which it is possible to obtain a continuous record of the amplitude of the wireless waves reflected from the ionized regions of the earth's atmosphere, is described. An optical system is used to separate the records made on the photographic paper by the first and second reflections. Attention is directed to the different types of signal fluctuations that may occur. Examples of an interference phenomenon between the two magneto-ionic components of the downcoming waves are described. The reflection coefficient of the ionized regions is discussed and a rapid method of finding the relationship between this coefficient and the frequency of the waves is described.

§ 1. INTRODUCTION

Some observations on the amplitude of wireless waves refracted by the ionized regions of the earth's atmosphere have been described in a previous paper⁽¹⁾. The majority of the results given in that paper were obtained by using the Breit and Tuve method of echo delineation, in conjunction with a cathode-ray oscillograph, in the well-known manner. The relative amplitudes of the refracted waves were measured by means of snapshot photographs of the trace on the screen of the oscillograph, these photographs being taken about once every minute. By this method it was possible to work out the general characteristics of the diurnal variation in amplitude of the downcoming waves. The method failed, however, to record the very rapid changes in amplitude that are known to occur, and it is obvious that, for a more complete study of the amplitude-variations, some form of continuous record is desirable. It is only from such a record that it is possible to find out the cause of these rapid variations. In this paper a simple modification of the Breit and Tuve method is described by means of which a continuous record of the amplitude of the downcoming waves may be obtained.

A method of recording which gives the amplitude as well as the equivalent height of reflection of the waves has been described by Hollmann and Kreielsheimer⁽²⁾. It is desirable for many reasons to know the equivalent height of reflection of the waves whose amplitude is being recorded, and in the method described below this is achieved by means of a second oscillograph on a separate record. Although this is an extra complication it is considered to add to the efficiency of the method.

The picture traced out on the screen of the cathode-ray tube when the Breit and Tuve method is being used is well known. In its simplest form it is similar to figure 1 (*a*), in which G represents the signal that has travelled to the receiver over the ground path while F_1 and F_2 are the echoes once and twice reflected from the upper region. The more complex cases that are commonly met with are shown in figures 1 (*b*), 1 (*c*) and 1 (*d*), which represent respectively single and double reflection from region E, a single reflection from region E together with single and double reflections from region F, and finally magneto-ionic splitting of the first and second reflections from region F. With the simple echo pattern shown in figures 1 (*a*) and 1 (*b*) continuous recording of the amplitude of each component is relatively simple, but with the more complex forms it is more difficult to obtain a record that will give a clear account of the behaviour of each component.

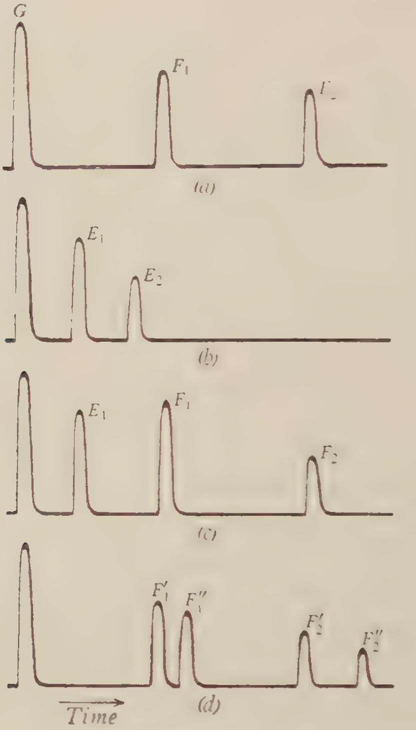

Figure 1.

§ 2. EXPERIMENTAL METHOD AND APPARATUS

For the simpler cases that have been mentioned above one naturally turns to a direct method of recording which is similar in some respects to that of Hollmann and Kreielsheimer. The trace on the screen of the cathode-ray oscillograph is arranged so that the time base is vertical while the displacements due to the ground ray and the echo are horizontal, as shown in figure 2 (*a*). An image of this trace is formed by a camera lens on a strip of photographic paper which is made to travel vertically upwards, as shown in figure 2 (*b*). The picture obtained is much improved by the use of two screens, one of which will allow only the top of the ground ray to appear, while the other prevents the time base from forming too dark an impression. Only a small section of the time base is exposed to the paper. As the amplitude of the first reflection varies it forms a trace of varying distance from the base line on the photographic paper, while the second reflection doubly exposes the paper and leaves a darker trace. An example of a record obtained with this method is shown in figure 3. This simple method of recording has been found to be very satisfactory for comparing the amplitude of the first reflection with that of the ground ray under simple conditions. It does not, however, give a very good trace of the second reflection, for this tends to become mixed up with the first reflection, especially when each of these components is varying considerably in amplitude. Since it is hoped that the most important results of this work will be the measurement of the total absorption suffered by the waves, to be effected by means of a comparison of the amplitudes of the first and second reflections, the method so far described was considered to be unsatisfactory and the following modification was introduced.

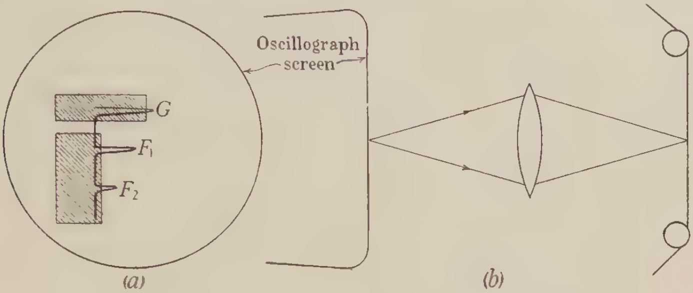

Figure 2.

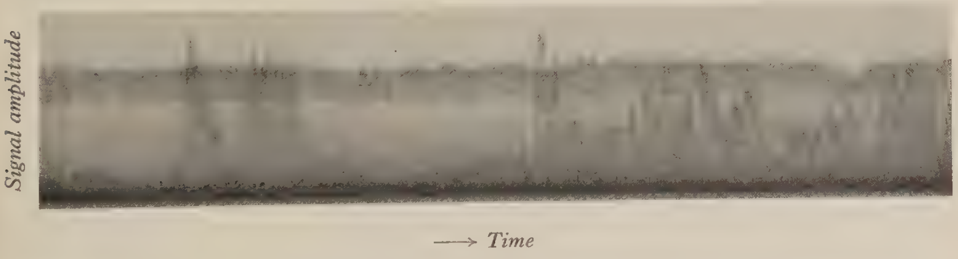

Figure 3. Comparison of ground ray and first reflection from region *F*.

In order that a record of the amplitude of the first and of the second reflections may be obtained on different parts of the photographic paper, an optical system consisting of eight prisms was introduced between the camera and the screen of the cathode-ray oscillograph. The trace on the screen of the oscillograph was arranged with the time base vertical as in the above example. Four exactly similar right-angled prisms are mounted as shown in figure 4 so that the image of the portion of the time base covered by prism *A* is displaced towards the right to a distance equal to half the width of one of the prisms. Vertically and immediately below this set of prisms is another similar set of four, arranged so that while the prism *A′* is directly beneath *A*, the two prisms *B′* and *C′* are displaced through half the width of a prism towards the left, and *D′* is displaced a whole width in this direction. With this arrangement the optical distance from all parts of the screen covered by *A* and *A′* to the camera lens is the same, while the top and bottom parts of the time base appear, when viewed from the camera, to be displaced to the right and left respectively. The vertical thickness of the prisms and the total length of the time base are fixed so that, for example, the first reflection may fall behind the prism *A* while the second reflection is behind *A′*. The thickness of the prisms, corresponding to a distance measured along the time base, is sufficient to allow a considerable change in the equivalent height of reflection of the waves, without the component considered moving out of the range covered by *A* or *A′*.

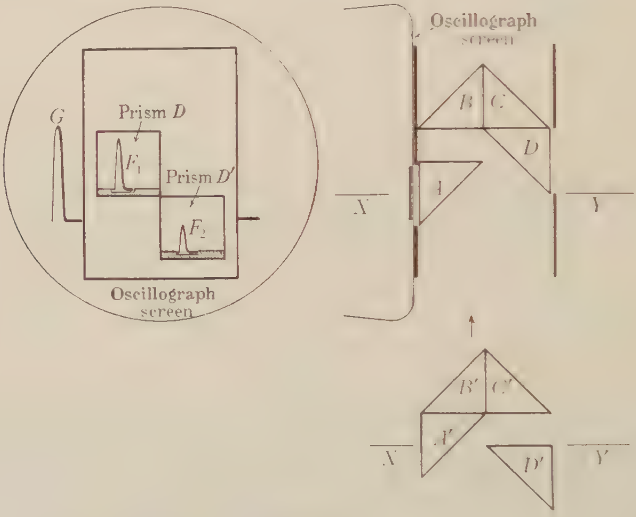

Figure 4.

The arrangement of the camera is, as before, with the paper moving vertically upwards. The alignment of the camera and the prisms is carried out by focusing the image of the time base on a ground-glass screen which replaces the photographic paper for this purpose. Opaque screens are used to eliminate excessive darkening of the paper by the time base.

By the use of an adjustable magnetic deflection of the cathode-ray beam the whole pattern on the screen of the oscillograph may be moved vertically upwards or downwards so that the positions of the reflected components may be adjusted with respect to the prisms *A* and *A′*. This adjustment may also be used for selecting the components to be recorded. For instance, when no second reflection is being received the pattern may be moved downwards so that the first reflection and the ground wave may be compared, or it may be adjusted so that reflections from region E are recorded. Examples of records obtained with this apparatus are shown in figures 5 to 10.

§ 3. DISCUSSION OF RESULTS

In the experiments that have been carried out with this apparatus the pulse signals were transmitted from the roof of the East Wing, King's College, London, and were received at the Halley Stewart Laboratory only six and a half kilometres away. In all cases, therefore, the waves are incident at practically normal incidence on the refracting regions of the upper atmosphere. At the receiving station reception was carried out on a superheterodyne receiver, for which the output, measured as a deflection on the screen of the oscillograph, was linearly related to the signal amplitude. It is of very great assistance in the elucidation of the records obtained with this apparatus, to receive the signals on some form of aerial which will discriminate between the two magneto-ionic components of the downcoming waves. It is well known that theoretically each of these components should be returned from the refracting regions circularly polarized, one component having a right-handed sense of rotation (the extraordinary ray) and the other a left-handed sense (the ordinary ray). A number of records have been obtained with a circularly polarized aerial of the type described by J. A. Ratcliffe and E. L. C. White(3). It may be mentioned that it has been found that usually the magneto-ionic components are not exactly circularly polarized but are elliptically polarized, the ratio of the axes being commonly of the order of 10 : 9.

Experiments with the apparatus have not been continued for a long enough period to enable an exhaustive study of the phenomena connected with the efficiency of reflection by the ionized regions to be made. There are, however, several features of the work which may be conveniently discussed to illustrate the method of recording. The results described below have been obtained with signal frequencies from 3 to 4 Mc./sec. The most obvious feature of the records is that they show up remarkably well the rapid variations of the amplitude of the reflected waves; it may be said that the amplitude of the reflected waves is rarely steady for more than a few seconds. At times the variation in amplitude is fairly slow, giving only two or three maxima per minute, but much more often it varies very rapidly. It is possible to recognize two distinct types of fading, type (*a*) being of a very regular nature which is associated with the interference of the two magneto-ionic components, and type (*b*) usually of a more irregular nature which occurs when only one of the magneto-ionic components is being received. Examples of type (*a*) can be seen in figures 5 and 7 while type (*b*) is exhibited in figure 8. It will be noticed that this method of recording has a distinct advantage over other methods for investigating fading by means of continuous-wave signals since interference effects can take place only between two downcoming components which have suffered approximately the same group-time delay. It is this time delay which determines whether two components will energize the receiving aerial practically simultaneously and so interfere, whereas it is the optical path difference which determines their relative phase angle.

Fading of type (*a*) is very satisfactorily accounted for as a phenomenon of interference between the extraordinary ray and the ordinary ray when there is a temporal change in the optical path difference for these two components, while the equivalent path difference between them is insufficient to cause them to be separated along the time base. Consider the example shown in figure 5. This record was obtained on the morning of May 8, 1934. Figure 6 shows the equivalent height measurements for May 8. Reflection of the extraordinary ray from region *F* had persisted throughout the night, while the ordinary ray had penetrated that region early in the previous evening. At 0435 G.m.t. it was once more returned from region *F*, its equivalent height of reflection being, to begin with, 500 km., while the equivalent height for the extraordinary ray was only 300 km. Within 20 minutes, however, the equivalent height for the former ray had fallen to almost exactly 300 km., so that the two components coalesced in the cathode-ray pattern. This can be seen very clearly on the record of equivalent heights which was taken at the same time as the amplitude record. If it be remembered that the equivalent-height record is not capable of revealing quite small differences in height between the two components, then it seems certain that although these two components (*F* ordinary and *F* extraordinary) are returned from almost exactly the same equivalent height; there is

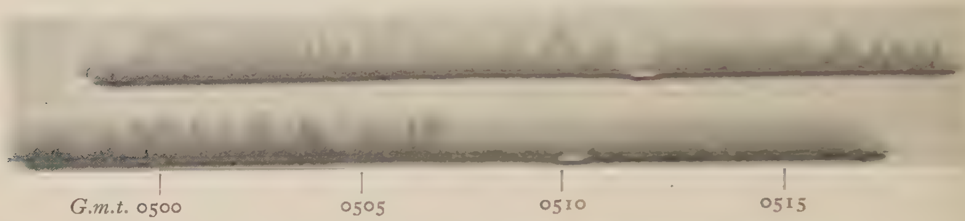

Figure 5. May 8, 1934. First and second reflection from region *F*.

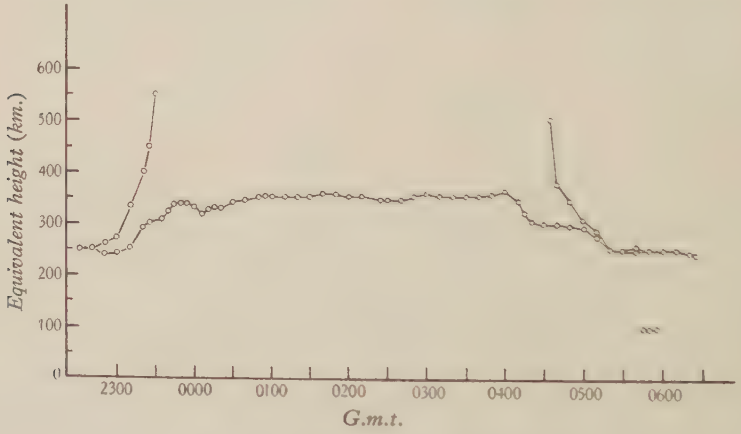

Figure 6. May 8, 1934. $f=3{\cdot}4$ Mc./sec.

still a small optical path difference between them which is changing with time so that the resultant intensity fades periodically as the waves go in and out of phase.

In figure 7 is shown another example taken at a slightly later time, 0530 G.m.t. The equivalent height record shows clearly that the extraordinary and ordinary rays tended to separate slightly from one another at this time, while the amplitude record shows the fading that resulted. As the optical path difference of the ordinary ray increases the amplitude varies in a periodic manner until, after about 7 minutes, these components are sufficiently resolved for each to leave its own trace.

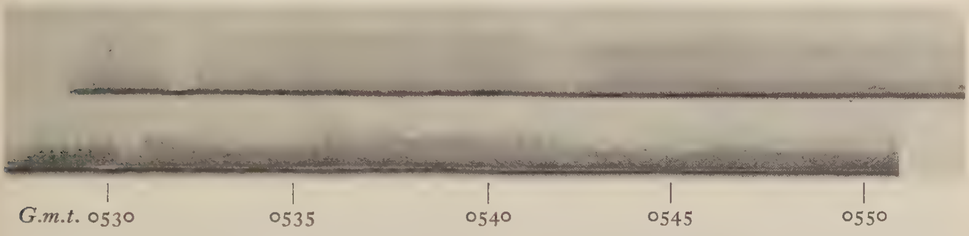

Figure 7. May 8, 1934. Ground ray and first reflection, region *F*.

With the known speed of movement of the photographic paper, time marks being made on the record every half hour, it is possible to calculate the number of maxima per minute and from this the rate of change of the optical path difference, $d(\delta P)/dt$, between the two components. These measurements are given in table 1 for the two examples quoted above, it being assumed that a change from one maximum to the next signifies a change in the optical path difference of one wave-length.

Table 1. Rate of change of optical path difference. Wave-length 88 m.

Time (G.m.t.)	Number of maxima per minute	$\frac{d}{dt}(\delta P)$ (km./min.)
0500	6·0	0·53
0507	10·0	0·88
0513	6·0	0·53
0517	1·5	0·13
0529	3·0	0·26
0532	5·5	0·48

It will be noticed, in the first example given above, that while the first reflection exhibits very regular maxima and minima the second reflection does not do so. There are two reasons which may be advanced to explain this. It will be remembered that the difference in group-time delay for the two components of the doublet after the second reflection is twice that for the first reflection. Thus, while the first two echoes may overlap sufficiently to produce interference, the second two may not do so. Then the reflection coefficient for the ordinary ray may be very different from that of the extraordinary ray, so that although the first reflections of both rays may be of comparable amplitude, the second reflection of one of them may be quite small. An examination of the records shows that both these causes are effective in preventing interference between the two components after second reflection.

Fading of type (*b*) is differentiated from type (*a*) chiefly by the fact that it occurs when only one of the two magneto-ionic components is being received. In such a case it is usually found that the fluctuations in amplitude are more irregular than those of type (*a*), but this is not necessarily so. During the night of May 7–8 for instance the extraordinary ray only was reflected from the *F* region and its amplitude variations could be very easily studied. In the early part of the night the variations were slow, but as the night advanced they became more rapid and irregular. There were several occasions on which very regular variations occurred. The records shown in figure 8 illustrate the fading that took place from 2340 to 0010 G.m.t. and from 0050 to 0120 G.m.t. A period of regular fading can be seen about 0120 G.m.t. In the same figure from 2340 to 0000 G.m.t. there is an example of a period when the amplitude of the second reflection was on occasions greater than that of the first reflection. There seems to be no definite relationship between the amplitude-variations of the first and second reflections.

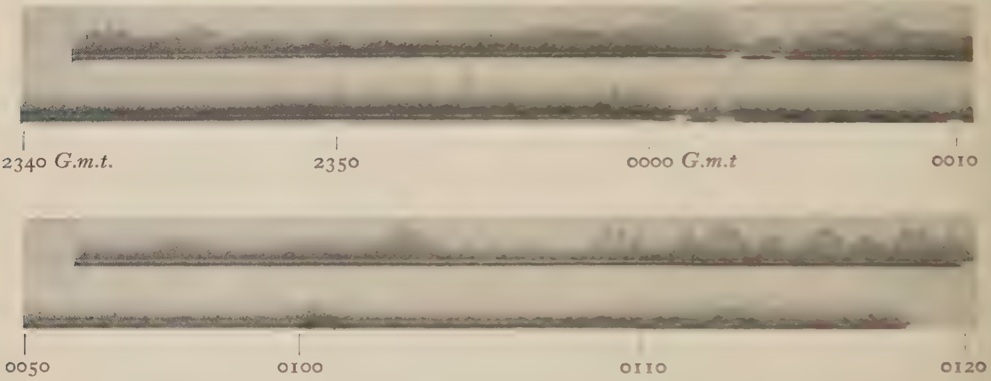

Figure 8. Extraordinary ray, region *F*.

The results during this period are analogous to those obtained by Appleton and Ratcliffe(4) in 1927 using waves of frequency about 0·75 Mc. sec. In their case the ordinary ray only from region *E* was observed during the night, the extraordinary ray being absent owing to absorption. From their observations it was concluded that "The changes in the downcoming wave are real intensity changes (as measured at the ground) and are not due to the rotation of a plane-polarized wave." Also "Although the cause of signal-variations has been traced mainly to intensity-fluctuations of the downcoming rays as measured at the ground we must not regard these fluctuations as being due to the alterations in the reflecting-power of a fixed flat surface, for other observations seem to indicate that these intensity-fluctuations are themselves the result of an interference mechanism the nature of which is at present somewhat obscure."

In the light of the present work something can be added to the conclusions of Appleton and Ratcliffe. Firstly, with the higher frequencies and for reflection from region *F*, when the extraordinary ray only is received during the night, or when the ordinary ray only is received during the day, the fluctuations in amplitude are similar to those found by Appleton and Ratcliffe with the lower frequencies and for reflection from region *E*. It is known that in the present investigation the fluctuations in amplitude frequently observed with the circularly polarized aerial, under either of the above conditions, show that the downcoming waves are always very nearly circularly polarized. The view that the changes in amplitude are caused by an interference mechanism is very strongly upheld by such an example as is shown in figure 8, where the maxima and minima are very similar to those found when interference between the two magneto-ionic components is known to be taking place. Although it is not yet certain how this interference mechanism operates, the variations in amplitude can be more satisfactorily accounted for in this way than by an assumption of very rapid variations in the total absorption suffered by the waves.

§ 4. BURSTS OF INTENSITY

Another interesting phenomenon which has been noticed on several occasions is one which may be called "bursts of intensity." It occurs during the daylight hours and has been observed with signal-frequencies of from 3 to 4 Mc./sec. During the daylight hours the ordinary ray only is normally received with frequencies of this order, the amplitude of the extraordinary ray being very small as a result of absorption. It is found that, while the amplitude of the ordinary ray may be for the most part quite small, sudden increases occur at fairly regular intervals in the intensity of this component. Most of the observations relate to the amplitude of the first reflection, but on one occasion, when the intensity of the first reflection was very great, the same phenomenon was found to occur in the case of the second reflection. A typical example of the phenomenon is shown in figure 9. This record, which was taken on March 28, 1934, from 1325 to 1345 G.m.t., shows the ground ray and the first reflection from region *F*. During most of the time the amplitude of the first reflection is small, but it increases at intervals of about 12 minutes to a very much greater value. This maximum usually lasts for about 3 minutes and is fairly steady throughout that period. On several other occasions the same phenomenon has been observed, and it is found that the length of the interval between

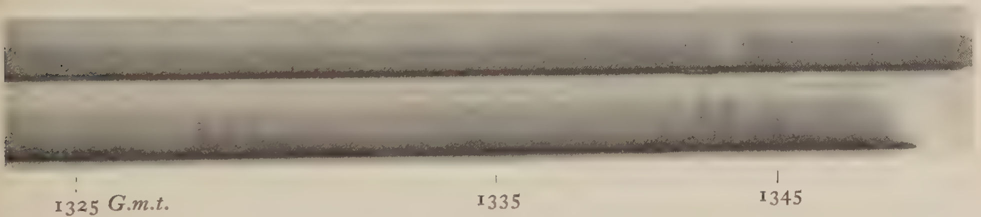

Figure 9. March 28, 1934. Ground ray and first reflection, region *F*.

bursts is usually of the same order. In table 2 are given data showing the regularity with which the bursts occur.

Table 2. Interval (minutes) between bursts of intensity

February 20, 1934 3·6 Mc./sec.	March 28, 1934 4 Mc./sec.		April 6, 1934 4 Mc./sec.
15	10	11	12·0
19	15	19	8·5
15	13	12	5·5
—	8	11	7·0
—	14	—	—
Average 16 minutes	Average 12·5 minutes		Average 8·6 minutes

Although perhaps seen to better advantage on the amplitude records, these bursts of intensity are of course evident on the (equivalent-height, time) records (P', t). On these records they show up as short periods during which second and even third reflections are obtained at times when only the first reflection is normally obtained. It would seem therefore that what actually happens is that the average intensity of each reflection is increased. It may be concluded therefore that for very short periods during the daylight hours the reflecting region, which is on the average a poor reflector, becomes a much better one.

§ 5. THE REFLECTION COEFFICIENT

It has been pointed out by Appleton and Ratcliffe(5) that if the radiating characteristics of the transmitting aerial are known, so that the relative amplitudes of the waves sent upwards to the ionized regions and of the ground wave can be found, then the decrease in the amplitude of the atmospheric wave due either to electron-limitation or to absorption can be expressed in terms of a reflection coefficient. This coefficient ρ was defined as

ρ

$$\rho = \alpha \frac{F}{G} \cdot \frac{d_1}{d_0},$$

where α is a constant depending on the transmitting aerial and upon the attenuation suffered by the ground wave, F and G are, respectively, the amplitudes of the downcoming wave from region F and the ground wave, and d_1 and d_0 are the distances travelled by these waves. The chief difficulty in the measurement of ρ by comparing F and G lies in the determination of α. This difficulty is immediately removed if it is possible to compare the amplitudes of the first reflection and the second reflection. Consider a wave that has suffered a single reflection at region F. This wave will be returned to the ground with an amplitude F_1. After reflection at the ground it will be reflected by the F region for the second time and returned to the ground with amplitude F_2. As has been shown above, the fact that these two echoes return to the receiver with different group-time delays makes it possible to measure the amplitude of each separately. In the case of vertical incidence the amplitude F_1 of the first reflection may be equated to $\beta\rho\, d_1$, where β is a constant,

α F, G d_1, d_0 F_1 F_2 β

whereas the amplitude F_2 of the second reflection will be $\beta\rho^2\rho_1/2d_1$. It may be assumed that the coefficient of the layer for the second reflection is the same as that for the first reflection, while the spherical waves will have travelled twice the distance d_1. In this expression ρ_1 is the reflection coefficient for the ground.

ρ_1

Thus from a measurement of F_1 and F_2 the ratio F_2/F_1 or $\rho\rho_1/2$ may be obtained. Since it is reasonable to assume that the coefficient for the ground is very nearly unity the value of ρ may be calculated directly from the equation

$$\rho = 2F_2/F_1.$$

A further extension of this reasoning is immediately possible. The amplitude G of the ground wave at the receiver will be related to the distance travelled by the equation

$$G = \delta/d_0.$$

Thus
$$\frac{F_1}{G} = \frac{\beta}{\delta}\cdot\frac{d_0}{d_1}\cdot\rho,$$

while
$$F_2/F_1 = \rho/2.$$

If therefore G, F_1 and F_2 are simultaneously observed, the constant

$$F_1^2/2F_2G \text{ or } (\beta/\delta).(d_0/d_1)$$

may be obtained. If this constant is observed at a time when it is possible to measure G, F_1 and F_2, then, with the same settings of the transmitter and receiver, ρ can be obtained at other times when only G and F_1 are obtainable, due allowance being made for any alteration in the distance travelled by the waves. In practice observations on either the ordinary or the extraordinary ray can be made, so that the reflection coefficient for either component can be obtained.

From what has been said above it is obvious that the average values of F_1 and F_2 must be used in calculating the reflection coefficient. In table 3 there are given values of this coefficient for the extraordinary ray during the night of May 7/8. It will be seen that in some cases the coefficient is greater than unity, a fact which supports the hypothesis that the variations in amplitude are due to rays scattered from irregularities in the refracting regions⁽⁶⁾.

Table 3. Reflection coefficient, May 7/8, 1934

Time (G.m.t.)	ρ	Time (G.m.t.)	ρ
2340	0·75	0206	0·60
2350	2·00	0220	1·42
0000	1·60	0240	0·40
0010	0·50	0255	0·43
0052	1·20	0300	0·30
0120	1·00	0320	0·25

§ 6. RELATIONSHIP BETWEEN THE REFLECTION COEFFICIENT AND FREQUENCY

P'
f

It has been amply demonstrated by Appleton that a vast amount of information about the ionized regions of the atmosphere can be obtained from an experimental determination of the relationship between the equivalent height P' of reflection of the waves and the frequency f. It will readily be appreciated that the study of the fading of the downcoming waves and of the general diminution in intensity due to absorption or electron-limitation might be aided by a similar line of attack. With this in mind the present method of recording has been used to determine what might be called the "reflection-coefficient, frequency" relationship. The ideal result would be obtained from a rapid determination of the reflection coefficient for a number of different frequencies following one another in rapid succession. Owing to the constant fading of the echoes, however, the amplitude must be recorded for sufficient time to allow a fair sampling of the average value for each frequency to be obtained. On the other hand it is desirable to cover the whole range of frequency in as short a time as is reasonably possible, in order to eliminate the possibility of major alterations in the atmospheric ionized regions. An examination of the fading records described above indicates that a good average value of the amplitude could be obtained in 5 minutes.

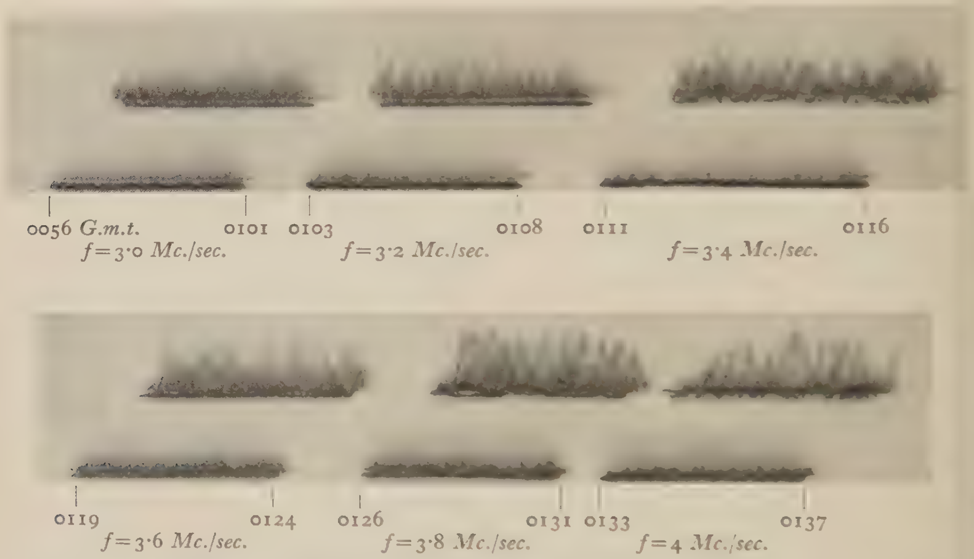

Figure 10. First reflection and second reflection, region *F*.

In figure 10 is shown a series of records of the amplitude of the first and second reflections from region F obtained during the night of May 14, 1934. The frequencies progress in steps of 0·2 Mc. sec. from 3 to 4 Mc. sec. These results were obtained with an ordinary inverted-L aerial. From the P', f curve which was taken simultaneously with this record it can be seen that both the extraordinary and the ordinary rays were present, with the same group-time delay, so that the amplitude recorded is the resultant of these two components. Measurements of the average values of the amplitudes of the first and second reflections show that the ratio F_1/F_2 is very nearly constant over this relatively small range of frequency. The average value for the ratio is 0·3. These results serve to illustrate the facility with which amplitudes may be compared for a number of different frequencies.

§ 7. ACKNOWLEDGMENT

I wish to express my thanks to Prof. E. V. Appleton for his encouragement and interest in this work. The work described in this paper was carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research.

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A BALANCE-DETECTOR FOR ALTERNATING-CURRENT BRIDGES

By C. R. COSENS, M.A.

Received May 26, 1934.

ABSTRACT. A balanced valve arrangement with a portable d.-c. galvanometer of pointer type is described for use as balance-detector in a.-c. bridge work. Over an extensive range of frequencies its sensitivity is comparable to that of a vibration galvanometer or telephone. The direction of deflection shows which way the bridge must be adjusted to secure a balance as in the case of a d.-c. bridge or electrodynamometer, but the false-zero effect found with the latter is absent. The arrangement could be adapted for use at radio frequencies.

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§ 1. INTRODUCTION

A perusal of Hague's *A.-C. Bridge methods*, in which descriptions and references are given for a large number of devices which are or have been used as balance-detectors, reveals that in this country at least the vibration galvanometer for low frequencies and the telephone for higher frequencies are in almost universal use, with a few instruments of dynamometer type. When increased sensitivity is required valve amplification may be used, but when the addition of an amplifier is once admitted we can use other devices which without such aid would be too insensitive. Experiments on rectifiers of various types led to the construction of a device, having certain advantages, which is herein described.

§ 2. COMPARISON OF KNOWN DEVICES

The vibration galvanometer is unsurpassed for use at a single fixed frequency if this is comparatively low, say < 250 c. sec. When measurements have to be made over even a small range of frequencies, retuning for each frequency takes time, whereas if a frequency-range of more than, say, 3 or 4 to 1 is wanted, it is usually necessary to change the coil and suspension, and while this operation may be easier on some makes of instrument than on others, it is an inconvenience with any instrument.

The telephone is insensitive at low frequencies, and the ear at very high ones, and in any case a silent room is desirable unless amplifiers are used with a loud-speaker. Furthermore, a visual indication is to be preferred to an aural one for accurate work.

An electrodynamometer, such as Sumpner's, has many advantages. It can be used throughout a long frequency-range without adjustment, and gives an indication of the sense of the change needed in the bridge to secure balance. These advantages are counterbalanced by the grave disadvantage that a false zero is obtained when the electrodynamometer is used on bridges of low impedance, owing to electromotive forces which are induced in the moving coil by the transformer action of the main field.

§ 3. SOME ELEMENTARY VALVE DEVICES

Many valve devices of well-known types can be used satisfactorily. For instance a valve amplifier may be followed by a Moullin voltmeter, or another rectifier, such as a crystal detector or Westinghouse rectifier. All suffer from the fact that for a small applied e.m.f. they necessarily operate as square-law devices, and although they can be made sufficiently sensitive by using amplifiers of high gain there is always the difficulty that any large error in balance is likely to damage the galvanometer unless unremitting attention is given to the necessity for shunting this instrument heavily until balance is nearly reached.

Alternatively a Sumpner electrodynamometer, with the moving coil connected in the anode circuit of a high-impedance valve (triode, screen-grid tetrode, or pentode) is sensitive and satisfactory, the false zero effect being almost completely eliminated; but similar results can be attained without using a reflecting instrument.

§ 4. VALVE-DYNAMOMETER PRINCIPLE

If a thermionic valve draws its anode supply not from a d.-c. battery but from an alternating source at the same frequency as that supplying the bridge, it will pass a certain rectified direct current which can be measured on a d.-c. galvanometer; this current will vary with the potential of the grid. If an alternating potential be applied to the grid from the detector branch points of the bridge, this rectified current will be increased or reduced, according as the grid potential is cophased or antiphased to the anode potential; and *the magnitude of this change is proportional to the first power*, not the square, *of the grid potential.*

In order to obtain sensitivity, it is desirable that the steady deflection of the d.-c. galvanometer should be balanced out by any well-known method, but there is then difficulty from wandering zero with change of supply voltage, a difficulty which can be overcome by using a second similar valve as a balancing-device, by which means we also obtain a doubling of the sensitivity.

Several devices of this nature were experimented with, and the circuit shown in outline in figure 1* was finally adopted as the most satisfactory.

§ 5. VALVE GALVANOMETER FOR ALTERNATING CURRENT

The author's device in its final form is shown diagrammatically in figure 1, the filament batteries and grid-bias arrangements being omitted for the sake of simplicity. Deferring consideration of the thin-line (grid) circuits, and confining attention to the thick lines, we may note a resemblance to the full-wave rectifier employed extensively for the high-tension supply of wireless receivers.

The primary of the transformer T_1 is supplied with alternating current of the same frequency as that used in the measurements on the bridge, and the two secondaries supply antiphased voltages to the anodes of valves V_1 and V_2. During one half-cycle current will flow in the valve, say V_1, whose anode is positive with respect to its filaments, returning via R_1 and causing a fall of potential from c to a; similarly, during the other half-cycle V_2 will pass current which returns via R_2 from c to b. If the two valves were identical these currents when averaged over a complete cycle would be equal, and a and b would be at the same mean potential. If the valves are not exactly similar, an adjustment of R_2 will secure the necessary equality of potential. Let this be referred to as the *no-signal state*, the signal being the e.m.f. across the detector branch points of the bridge. In this state a d.-c. galvanometer G connected between a and b will carry no current, when the current is averaged over a complete cycle. To prevent pointer-wobble at low frequencies due to alternating current in the galvanometer, the choke-condenser arrangement *Ch*, *C*, in figure 1 is adopted.

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* British patent specification no. 385,982 (January, 1933).

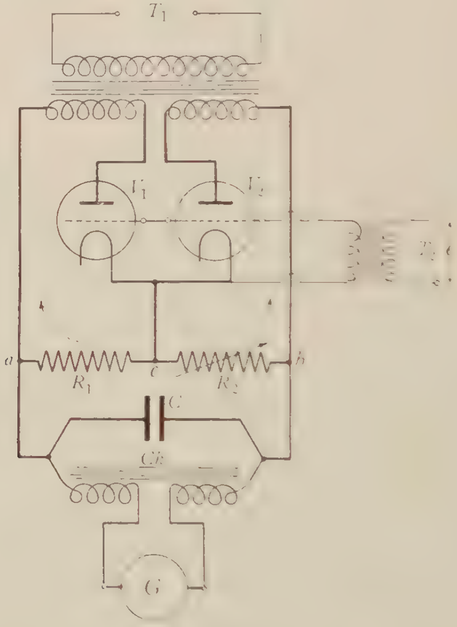

Figure 1.

If now the terminals of the grid transformer T_2 be connected to the branch points of the bridge, across which we suppose a potential-difference e to exist, a deflection of the galvanometer G will in general result. Suppose first that the phase of e is such that the grid and anode of V_1 reach their maximum positive values simultaneously. Then during the half-cycle in which the anode of V_1 is positive its grid also is positive, and it passes a larger anode current than in the no-signal state. The anode of V_2 being negative no current flows in V_2. During the next half-cycle the anode of V_1 is negative and this valve is therefore inoperative, but the anode of V_2 is now positive and it passes a current; but since the grid of V_2 is now negative, it passes less current than it did in the no-signal state. The effect of the potential e is therefore to cause V_1 to pass more current, and V_2 to pass less, than in the no-signal state, and this difference of currents causes a difference in the potential-drops *ca* and *cb*, so that *a* and *b* are no longer at the same mean d.-c. potential and a current flows in the galvanometer G. It is easily seen that a reversal of e will reverse the galvanometer deflection.

It is shown in the Appendix that if e is not in phase with the anode voltage of one of the valves, but lags behind it by an angle ϕ, the galvanometer current is approximately proportional to $e \cos \phi$.

ϕ

§ 6. FREQUENCY-SELECTIVITY

The device is frequency-selective; though not absolutely free from deflection by e.m.f. of frequencies other than that supplied to T_1, owing to inexact matching of valves etc., the frequency-selectivity is ample for most purposes. It is interesting to note that it is possible to make the device sensitive to all frequencies except a specified frequency, to which it does not respond. For this purpose the grids are supplied as shown in the figure, but both anodes are supplied from one half of the secondary of T_2, being connected together. If the valves were exactly similar the effect of e applied to the grids would be to affect both valves equally, and no difference of anode currents would exist to deflect G. This might be useful in certain cases, e.g. for the indication of nerve-response, the nerve being stimulated by alternating current, and the anodes of the valves being supplied at the stimulation frequency. The device would be sensitive to the nerve response, which would not be at exactly stimulation frequency, but the effects of leakage of stimulation current would be very much reduced.

§ 7. PHASE-SELECTIVITY

Like all instruments having the characteristics of a dynamometer, i.e. in which the instantaneous deflecting torque on the indicator is dependent on the product of two quantities and not on the square of a single quantity, the device is phase-selective; that is to say that it indicates the component of e in phase with the main supply to the valve anodes via T_1. Thus if T_1 be connected across the a.-c. source which supplies the bridge the device will be sensitive to errors of resistance-adjustment but not of reactance-adjustment; to obtain sensitivity to errors of reactance-adjustment a phase-shift of approximately $\pi/2$ must be introduced. Any well-known phase-shifting device may be used, such as a phase-shifting transformer or

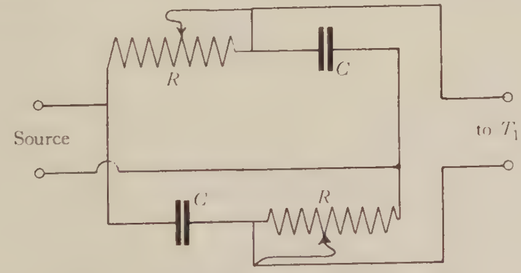

Figure 2. (Resistances R are ganged.)

a resistance-capacity combination; one of the best of these, described in *The Cathode-Ray Oscillograph in Radio Research* by Watson-Watt, Herd, and Bainbridge-Bell, is shown in figure 2, in which the two capacities C are equal and the two resistances R are ganged so as to be always equal to one another. Provided that the load on this phase-shifter is of impedance high compared to that of the C, R combination, there is little change of magnitude in the output p.d. and a phase-shift of about 120° is readily obtainable.

The phase-shifter may be introduced between the source and the input terminals of T_1, or between the detector branch points of the bridge and the input terminals of T_2, or between the output terminals of T_2 and the valve-grids, the last-mentioned arrangement being perhaps the best.

The balancing of the a.-c. bridge is then simplified, the procedure being as follows. With zero phase-shift, the resistance of the bridge is adjusted until balance is indicated. A phase-shift of about $\pi/2$ is then introduced and the reactance is adjusted. These two operations are repeated until balance is obtained in both for the same setting of resistance and reactance. The ability to adjust resistance and reactance separately enables the final adjustment to be reached with great rapidity.

§ 8. FREQUENCY LIMITS AND SENSITIVITY

The device can be used at almost any frequency if suitable components are employed. If T_1, T_2 are transformers of the type used in commercial audio-frequency amplifiers, the frequency limits are those at which the transformers cease to operate efficiently. If specially designed transformers are used there seems to be no reason why the method could not be adapted for use at radio-frequencies.

Owing to the balancing out of the mean anode currents (of the order of say 2 mA.) of the valves, the balance is not much affected by voltage changes, and G may be a centre-zero unipivot galvanometer giving full-scale deflection for 12 microamperes, suitable shunts being used for the preliminary adjustments. The ratio of the sensitivity of the twin-valve arrangement described to that of an unbalanced arrangement would then be as 12 μA. is to 2 mA., or 1000 : 6, even if the e.m.f. e were applied to the grid of only one valve, the grid of the other being maintained at constant potential. But as the two valves operate differentially on the galvanometer G, which in effect measures the difference of their anode currents, the sensitivity is doubled and becomes 2000 : 6, or say 300 times as great as with an unbalanced arrangement. For this it is necessary to have a fine adjustment of the balancing resistance R_2; and experiment shows that if an attempt is made to balance a similar circuit with one valve replaced by a resistance, the balance is rapidly upset by small changes of supply voltage. However, with the two-valve arrangement described the device is to a large extent self-compensating for this sort of variation.

In the completed instrument sensitivity is almost independent of frequency, and is comparable with that of a vibration galvanometer at 50 c./sec. and with that of a telephone at 500 c./sec.

§ 9. COMMERCIAL FORM OF INSTRUMENT

While the arrangement shown in figure 1 can be set up temporarily and made to work, with the component parts widely spread over the laboratory table, certain difficulties arise when the whole is assembled in a metal screening-box of reasonable size. These difficulties have now been overcome and several refinements have been added, such as a fine adjustment to the rheostat R_2, balanced and screened transformers for T_1 and T_2, with primary tappings to suit a source and bridge of varying impedances, a self-contained unipivot galvanometer with suitable shunts to reduce the sensitivity during preliminary adjustments, and a properly filtered automatic grid-bias.

The instrument is now made in a commercial form by the Cambridge Instrument Co. Ltd.

APPENDIX

APPROXIMATE MATHEMATICAL ANALYSIS

Let $\mu = [\partial v_a / \partial v_g]_{i_a}$ and $\rho = [\partial v_a / \partial i_a]_{v_g}$ for each valve and let $R_1 = R_2 = R$.

Let i, v_a, v_g be the instantaneous anode current, anode potential and grid potential, respectively.

Assume that

$$i = \frac{1}{R+\rho}(v_a + \mu v_g) \quad [v_a > 0]; \qquad i = 0 \quad [v_a < 0].$$

For valve V_1, let $v_a = V \sin \omega t$; $v_g = E \sin (\omega t + \phi)$.

Then $$i_1 = \frac{1}{R+\rho}(V \sin \omega t + \mu E \sin [\omega t + \phi]) \qquad [0 < \omega t < \pi],$$

$$i_1 = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad [\pi < \omega t < 2\pi].$$

Writing I_1 for the mean value of i over a cycle, and putting $\theta = \omega t$ we have

$$I_1 = \frac{1}{2\pi}\left[\frac{1}{R+\rho}\int_0^{\pi}[V + \mu E \cos \phi] \sin \theta \, d\theta + \int_0^{\pi}[\mu E \sin \phi] \cos \theta \, d\theta + \int_{\pi}^{2\pi}(0)\, d\theta\right],$$

$$I_1 = \frac{1}{\pi [R+\rho]}[V + \mu E \cos \phi].$$

Similarly for the mean anode current of V_2 we have

$$I_2 = \frac{1}{\pi [R+\rho]}[- V + \mu E \cos \phi].$$

Therefore $$I_1 - I_2 = \frac{2}{\pi [R+\rho]} \mu E \cos \phi.$$

Now $(I_1 - I_2)$ must flow from b to a, i.e. through the galvanometer of resistance g, shunted by $2R$. Hence the galvanometer current

$$= \frac{2R}{g+2R}(I_1 - I_2)$$

$$= \left[\frac{2R}{g+2R}\frac{1}{R+\rho}\frac{2\mu}{\pi}\right] E \cos \phi.$$

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SPECIAL CASES OF THE MUTUAL INDUCTANCE BETWEEN CIRCLES, WITH SOME PRACTICAL APPLICATIONS*

By F. H. LLEWELLYN, Ph.D., Birkbeck College

Communicated by Dr H. R. Nettleton, April 26, 1934.

ABSTRACT. This paper contains the results of some practical work on the mutual inductance between coils. It shows that equations relating to the ideal case of circles can be applied to multi-layered coils under conditions giving (*a*) constancy of the mutual inductance between twin coils connected in conjunction and a smaller coil sliding on a rod through the centre of symmetry *O* of the pair, for certain distances between the twin coils and certain angles made by the rod with their planes; (*b*) proportionality between mutual inductance and displacement for the same coils if the twin coils are connected in opposition; (*c*) proportionality between mutual inductance and angle if a large central coil is rotated about a diameter through the centre of symmetry *O* of the twin coils, for certain conditions as to the distances between the twin coils and the ratios borne by the radius of the central coil to that of either of the twin coils: and (*d*) proportionality between mutual inductance and the sine of the angle between the twin coils and a solenoid rotating symmetrically between them, for given dimensions of the solenoid.

The paper also gives a simple method for determining the absolute magnetic moment of a magnet, in which the need for corrections for the dimensions of the magnet is avoided.

§ 1. THEORY

a CONSIDER two coaxial circles *A* and *B*, each of radius *a*, separated one from
x the other by a distance $2x$, figure 1. *O* is their centre of symmetry through
θ which passes a line *MN* making an angle θ with the planes of the circles.
l With its centre along this line, at a distance *l* from *O*, is another circle *C* of smaller
α radius α lying in a plane perpendicular to *MN*. The distances of *O* from the peri-
s, ψ, ϕ phery of *A* (or *B*) and *C* are *r* and *s* respectively, while ψ and ϕ are the angles
M_J subtended by the radii of *A* and *C* respectively at *O*. The mutual inductance M_J
between *A* and *B* in conjunction (i.e. with their magnetic fields in the same direction)
and *C* is given by

$$M_J = Gq \sum_{n=1}^{n=\infty} \frac{2}{n(n+1)} \left(\frac{s}{r}\right)^{n-1} P_n'(\cos\psi)\, P_n'(\cos\phi)\, P_n(\sin\theta) \quad \text{......(1)},$$

q, G where $q = \pi\alpha^2$ and is the area of the small circle *C*; $G = t.2\pi a^2/r^3$ and is the
t galvanometer constant of *A* and *B* in conjunction at the origin *O*; *t* is the total
number of turns on *A* and *B* together, if these are considered as coils with the turns

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* Part of a thesis accepted for the degree of Doctor of Philosophy, by the University of London.

of each coincident; P_n is the Legendre function of the first kind of order n, P_n' its first differential coefficient and n is an odd positive integer*.

For M_P, the mutual inductance between A and B in opposition and C, equation (1) holds except that n is now an even positive integer. G, however, is still the galvanometer constant of A and B in conjunction. In practical work it is easier to deal with the relationship in terms of the radii and separation of the circles than in terms of functions of the angles they subtend, so it is convenient to expand equation (1) in terms of x, a, l and α as follows:

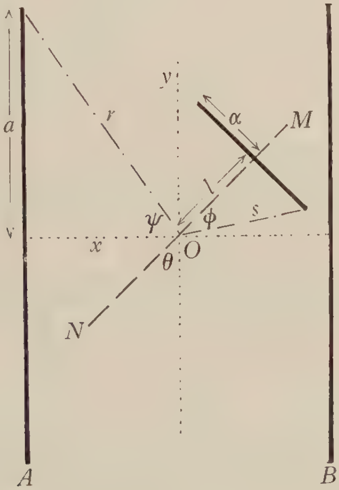

Figure 1.

$$
\begin{aligned}
M_J/Gq = {} & \frac{1.2}{2}\sin\theta \\
& + \frac{3.4}{2}\cdot\frac{1}{r^4}\left[x^2-\frac{a^2}{4}\right]\left[l^2-\frac{\alpha^2}{4}\right]P_3(\sin\theta) \\
& + \frac{5.6}{2}\cdot\frac{1}{r^8}\left[x^4-\frac{3}{2}x^2a^2+\frac{a^4}{8}\right]\left[l^4-\frac{3}{2}l^2\alpha^2+\frac{\alpha^4}{8}\right]P_5(\sin\theta) \\
& + \frac{7.8}{2}\cdot\frac{1}{r^{12}}\left[x^6-\frac{15}{4}x^4a^2+\frac{15}{8}x^2a^4-\frac{5}{64}a^6\right][F_7(l,\alpha)]\,P_7(\sin\theta) \\
& + \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\
& + \frac{n(n+1)}{2}[F_n(x,a)]\,[F_n(l,\alpha)]\,[1/r^{2(n-1)}]\,P_n(\sin\theta) \qquad \dots\dots(2),
\end{aligned}
$$

where n is odd and $$F_n(x,a)=\frac{2}{n(n+1)}r^{n-1}P_n'(\cos\psi) \qquad \dots\dots(2a),$$

and $$F_n(l,\alpha)=\frac{2}{n(n+1)}s^{n-1}P_n'(\cos\phi) \qquad \dots\dots(2b).$$

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* *Proc. Phys. Soc.* **44**, 198 (1932).

The first few terms of M_P/Gq are as follows:

$$\begin{aligned} M_P/Gq = {} & \frac{2\cdot3}{2}\cdot\frac{1}{r^2}\, xlP_2(\sin\theta) \\ & + \frac{4\cdot5}{2}\cdot\frac{1}{r^6}\left[x\left(x^2-\frac{3}{4}a^2\right)\right]\left[l\left(l^2-\frac{3}{4}\alpha^2\right)\right]P_4(\sin\theta) \\ & + \frac{6\cdot7}{2}\cdot\frac{1}{r^{10}}\left[x\left(x^4-\frac{5}{2}x^2a^2+\frac{5}{8}a^4\right)\right][F_6(l,\alpha)]\,P_6(\sin\theta) \\ & + \frac{8\cdot9}{2}\cdot\frac{1}{r^{14}}\left[x\left(x^6-\frac{21}{4}x^4a^2-\frac{35}{8}x^2a^4-\frac{35}{64}a^6\right)\right][F_8(l,\alpha)]\,P_8(\sin\theta) \\ & + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad \ldots\ldots(3). \end{aligned}$$

The direct evaluation of $F_n(x, a)$ or the corresponding $F_n(l, \alpha)$ is laborious if n is large, but it can be shown by a theorem of spherical harmonics that if n is odd

$$F_{n+1}(x, a) = n\int_0^x F_n(x, a)\,dx \qquad \ldots\ldots(4),$$

and if n is even

$$F_{n+1}(x, a) = n\int_0^x F_n(x, a)\,dx + (-\tfrac{1}{2})^{n/2}a^n\,\frac{1\cdot3\cdot5\,(n-1)}{[(n-2)/2]!} \qquad \ldots\ldots(5),$$

whence each term can be obtained from its preceding term.

Lines of isomutual inductance, A and B in conjunction. Examination of equation (2) shows that if x^2/a^2 is made equal to $\frac{1}{4}$—the well-known Helmholtz criterion—its second term vanishes. If we now choose θ so that $P_5(\sin\theta)$ is zero ($\theta = 64°\ 59'$ or $32°\ 35'$) then the third term also disappears and any variation from constancy of $M_J/Gq\sin\theta$ depends on the fourth and succeeding terms. We can, however, make the second and third terms of equation (2) vanish in another way. The distance between A and B can be chosen so that $x^4 - \frac{3}{2}x^2a^2 + a^4/8$ is zero ($x^2/a^2 = 0{\cdot}08856$ or $1{\cdot}41144$, the former being the useful solution) and θ can be chosen so that $P_3(\sin\theta) = 0$ ($\theta = 50°\ 46'$). Once again departure from constancy of $M_J/Gq\sin\theta$ depends on the fourth and following terms. In either of these arrangements it can be shown by substituting the appropriate values of θ and x that further terms are negligible. Practical work described later bears out this conclusion.

Lines of constant inductance-gradient, A and B in opposition. In a similar way if in equation (3) we make the conditions such that $x^4 - \frac{5}{2}x^2a^2 - \frac{5}{8}a^4 = 0$ and $P_4(\sin\theta) = 0$, then M_P/Gq is proportional to l. The useful value of x^2/a^2, viz. $0{\cdot}281754$, taken with $\theta = 19°\ 53'$ or $\theta = 59°\ 27'$ gives us conditions under which equal shifts of C along MN, figure 1, give equal changes in the mutual inductance between A and B in opposition and C. As before, terms after the third can be shown to be negligible.

Effect of multiplicity of layers. In the above discussion A and B have been taken as single-turn circles, or as coils all of whose turns are coincident. Such coils cannot be constructed in practice, but by treating the problem as in a previous paper* we can find the correcting factors f_1, f_2, f_3, for the first three terms of equation (2) due to the presence of multiple layers. If $2b$ is the axial breadth and $2d$ the radial depth of A or B,

f_1, f_2, f_3
b, d

$$f_1 = 1 - \frac{1}{2}\cdot\frac{b^2}{a^2}\cdot\frac{a^4}{r^4}\left(1 - 4\frac{x^2}{a^2}\right) + \frac{1}{3}\cdot\frac{d^2}{a^2}\cdot\frac{a^4}{r^4}\left(1 - \frac{11}{2}\cdot\frac{x^2}{a^2} + \frac{x^4}{a^4}\right) \quad \text{......(6)},$$

$$f_2 = 1 - \frac{5}{2}\cdot\frac{b^2}{a^2}\cdot\frac{a^4}{r^4}\left(1 - 12\frac{x^2}{a^2} + 8\frac{x^4}{a^4}\right)\Big/\left(1 - 4\frac{x^2}{a^2}\right)$$
$$+ 2\frac{d^2}{a^2}\cdot\frac{a^4}{r^4}\left(1 - \frac{53}{4}\cdot\frac{x^2}{a^2} + \frac{34}{3}\cdot\frac{x^4}{a^4} - \frac{2}{3}\cdot\frac{x^6}{a^6}\right)\Big/\left(1 - 4\frac{x^2}{a^2}\right) \quad \text{......(7)},$$

$$f_3 = 1 - \frac{35}{6}\cdot\frac{b^2}{a^2}\cdot\frac{a^4}{r^4}\left[1 - 24\frac{x^2}{a^2} + 48\frac{x^4}{a^4} - \frac{64}{5}\cdot\frac{x^6}{a^6}\right]\Big/\left[1 - 12\frac{x^2}{a^2} + 8\frac{x^4}{a^4}\right]$$
$$+ 5\frac{d^2}{a^2}\cdot\frac{a^4}{r^4}\left[1 - \frac{151}{6}\cdot\frac{x^2}{a^2} + 55\frac{x^4}{a^4} - \frac{92}{5}\cdot\frac{x^6}{a^6} + \frac{8}{15}\cdot\frac{x^8}{a^8}\right]\Big/\left[1 - 12\frac{x^2}{a^2} + 8\frac{x^4}{a^4}\right] \quad \text{......(8)}.$$

The correcting factor f_1 for the fundamental term has not the importance in this investigation that it has in absolute galvanometry since the corrected fundamental term is measured experimentally. Now either f_2 or f_3 can be made to be unity (and so the second or third terms can be made independent of multiplicity of layers) if b/d is made 0·928 or 0·957 when $x^2/a^2 = 0{\cdot}25$ or 0·08856 respectively. For practical purposes, if the twin coils are constructed with a square cross-section, whose side is small compared with the mean radius of the windings, the effect of multiplicity of layers is negligible. Now for each position of constant mutual inductance one term is made independent of multiplicity of layers by the shape of the windings of A and B and so can be made to vanish for the value of x/a appropriate to a coil whose turns are coincident while the other term, which vanishes by choice of θ, vanishes whether A and B possess multiple layers or not. Hence lines of isomutual inductance can be obtained even when the main coils are multi-layered.

The mutual inductance between twin coils A and B and a solenoid S. If the coil C is replaced by a solenoid S lying symmetrically with its axis on MN, it is easy to show by the integration of the effect of all its elements that the mutual inductance M_θ between twin coils A and B and S is given by

M_θ

$$M_\theta/GQ = \frac{1.2}{2}\sin\theta$$
$$+ \frac{3\cdot 4}{2}\cdot\frac{1}{r^4}\left[x^2 - \frac{a^2}{4}\right]\left[\frac{L^2}{3} - \frac{\alpha^2}{4}\right] P_3(\sin\theta)$$
$$+ \frac{5\cdot 6}{2}\frac{1}{r^8}\left[x^4 - \frac{3}{2}x^2a^2 + \frac{a^4}{8}\right]\left[\frac{L^4}{5} - \frac{L^2\alpha^2}{2} + \frac{\alpha^2}{8}\right] P_5(\sin\theta)$$
$$+ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$+ \frac{n(n+1)}{2}\cdot\frac{1}{r^{2(n-1)}}\left[\frac{2}{n(n+1)} r^{n-1} P_n'(\cos\psi)\right]$$
$$\times\left[\frac{2}{n(n+1)(n+2)} s_1^{n-1}\frac{P'_{n+1}(\cos\phi_1)}{\cos\phi_1}\right] P_n(\sin\theta) \quad \text{......(9)},$$

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* *Proc. Phys. Soc.* **44**, 201 (1932).

L, s_1 where $2L$ is the length of the solenoid, s_1 is the distance from O to the periphery ϕ_1 of the outside turn, ϕ_1 is the angle subtended by the radius of the outside turn at O, Q and Q is the total area of the solenoid.

Design of a solenoid to measure θ. It is possible, for all values of x/a and θ, to make the second term of equation (9) vanish by making $L^2/3$ equal to $\alpha^2/4$. If α is small with respect to a, then the importance of the third and successive terms is small and hence, for a solenoid constructed so that its total length is $\sqrt{3}$ times its radius and arranged to lie symmetrically with its axis on MN, the mutual inductance M_θ between it and A and B in conjunction is proportional to $\sin\theta$, and M_θ/M_{90} gives $\sin\theta$, where M_{90} is the value of M_θ when $\theta = 90°$. Such a solenoid can conveniently be called an angle solenoid. Its use in measuring angles will be justified practically later.

m F *The measurement of the absolute moment of a magnet.* If a magnet of moment m lying along MN with its centre at O replaces S, then the flux F threading A and B is given to a high order of accuracy by

$$F = mG\sin\theta \qquad \text{......(10)},$$

when its magnetic axis lies along a line of isomutual inductance*.

If S also lies at this angle

$$M_\theta = GQ\sin\theta \qquad \text{......(11)}.$$

G_s, M_s If now the mutual inductance between S and a standard solenoid of constant G_s is M_s, then $Q = M_s/G_s$ and combining these expressions we find that

$$m = \frac{F}{M_\theta}\left(\frac{M_s}{G_s}\right) \qquad \text{......(12)}.$$

The correcting factor f_1 for non-coincidence of turns, being involved in both (10) and (11), has been eliminated and equation (12) gives the absolute moment of a magnet directly in terms of a flux, a ratio of two mutual inductances and a solenoid constant.

§ 2. EXPERIMENTS ON THE MUTUAL INDUCTANCE BETWEEN TWIN COILS IN CONJUNCTION AND A SMALL COIL

The apparatus. This was arranged as in figure 1. Practical details are shown in figure 2. The coils A and B were wound on formers of dexonite. The coil channels were square in cross-section, in accordance with the conditions laid down in § 1 for the correction of the effect of multiplicity of layers. The radial depth and axial breadth were 3·6 cm. Each coil had 504 turns of double-silk-covered copper wire (s.w.g. 16) of mean diameter $32{\cdot}8_2$ cm. The coil C used in this section was of axial length 0·8 cm. It consisted of 1100 turns of double-silk-covered copper wire (s.w.g. 38). As its total area q was 2290 cm², its average diameter was $1{\cdot}62_8$ cm. The coil was arranged to slide axially on a wooden rod held in a circular ebonite framework so that, when the framework was rotated on its spindles EE, the rod always passed through the centre of symmetry O, of A and B. The displacement of C along the rod was measured by a scale marked on the rod. The angle θ made by the rod with the planes of A and B could be estimated by means of a pointer F, but was accurately determined by the ratio of the mutual inductances between A and B in conjunction and C at zero displacement, first at the given angle and then when θ was 90°. Since C was small this ratio gave $\sin\theta$. A check coil wound on the circular ebonite framework was used to find out if θ had been altered accidentally during a series of readings for the same angle. The check was easily performed by measuring the mutual inductance between this coil and A and B in conjunction, at intervals during the readings.

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* See also *Proc. Phys. Soc.* **42**, 506 (1930).

Method. A and B were set co-axially and symmetrically about the axis EE of the circular framework and locked in this position by means of distance pieces. Accuracy of setting was checked by measuring the mutual inductance between C and A, B for a number of symmetrical positions of C, the coils A, B being sometimes in conjunction and sometimes in opposition. The rod was then set at angles ranging from $\theta = 0°$ to $\theta = 90°$ inclusive, and a series of readings were taken of the mutual inductance M_J between C and A, B in conjunction for displacements varying from + 10 cm. to − 10 cm. They were measured on a Campbell mutual inductometer of range 0 to 11000 μH. either by Hartshorn's modification of Felici's a.-c. method* or by a d.-c. method with a ballistic galvanometer. A.-c. readings were standardized by comparison with occasional d.-c. readings. Figures 3 to 8 show M_J plotted against l, the displacement, for various angles θ and for separations of A and B ranging between 7·5 cm. and 20 cm. approximately.

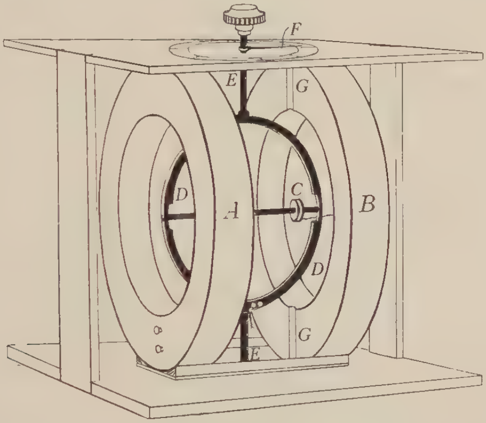

Figure 2.

The straightness of the lines obtained in figures 5 and 7 shows the constancy of M_J when θ and x/a are correctly chosen. This constancy is shown in a different way in figures 9 and 10, in which M_J is plotted against the angle θ for various displacements of C. The position of constancy for a value 0·089 of x^2/a^2 and the two positions of constancy for which $x^2/a^2 = 0{\cdot}25$ are clearly shown. This method probably gives the more accurate way of judging the exact angle for which constancy of inductance is achieved. The actual figures taken show that for $x^2/a^2 = 0{\cdot}25$ and

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* *J. Sci. Inst.* **2**, 145 (1925).

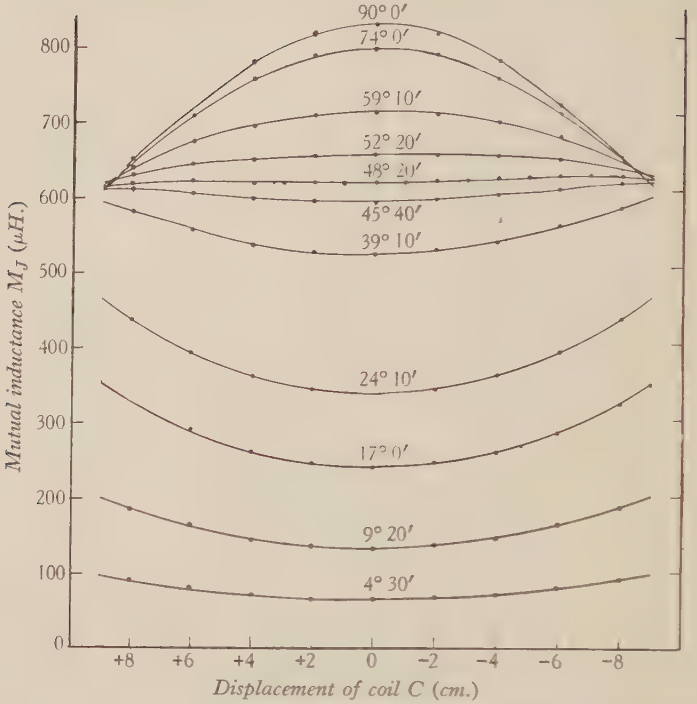

Figure 3. Coils *A* and *B* 7·40 cm. apart, in conjunction. $x^2/a^2=0{\cdot}051$. *C* small.

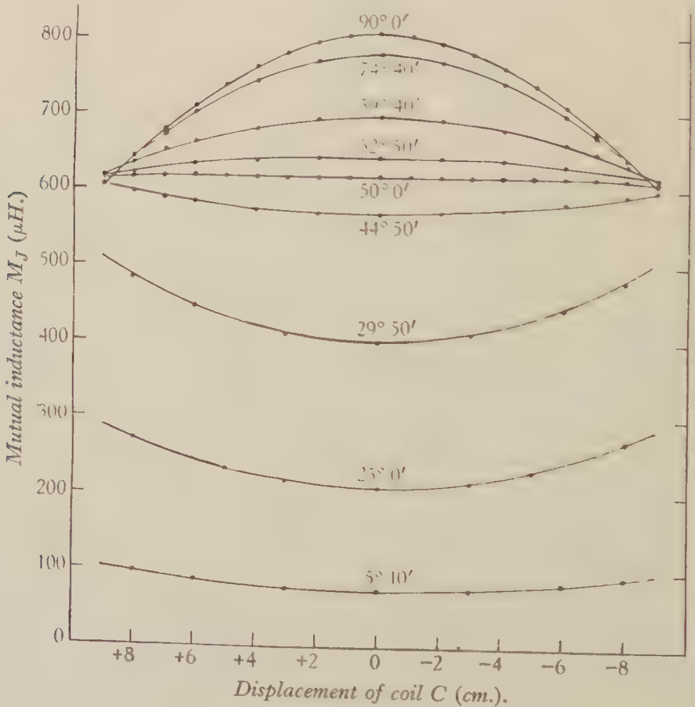

Figure 4. Coils *A* and *B* 8·48 cm. apart, in conjunction. $x^2/a^2=0{\cdot}067$. *C* small.

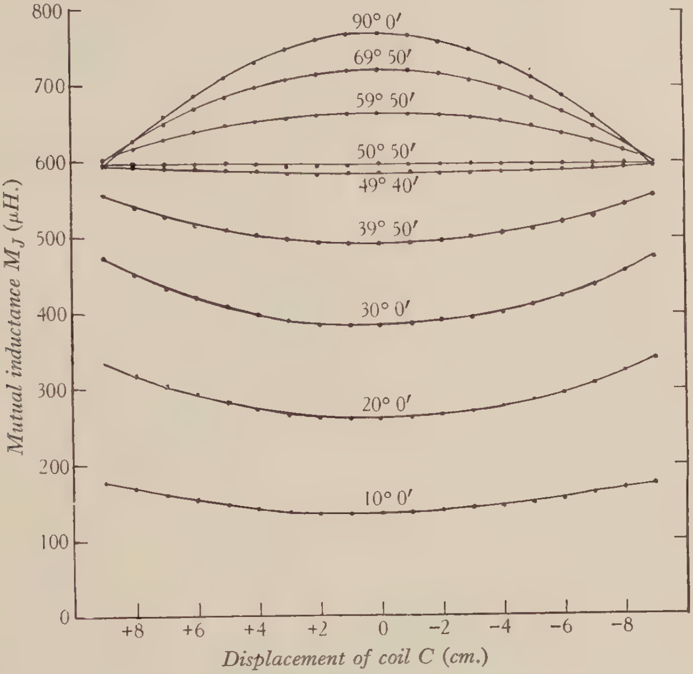

Figure 5. Coils A and B 9·81 cm. apart, in conjunction. $x^2/a^2=0{\cdot}089$. C small.

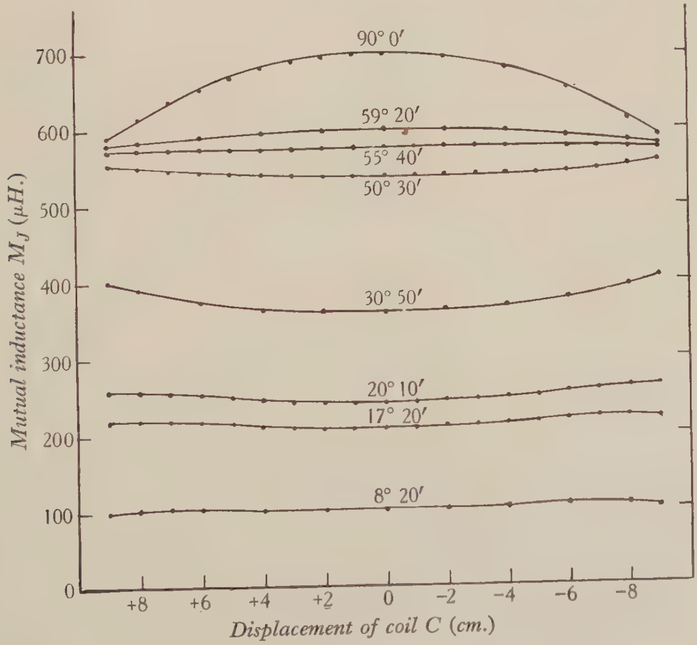

Figure 6. Coils A and B 13·1 cm. apart, in conjunction. $x^2/a^2=0{\cdot}159$. C small.

$\theta = 65°$ or $33°$ the differences between the highest and the lowest readings were 0·65 and 1·6 per cent respectively over a range of ± 8 cm. Over the same range at $x^2/a^2 = 0{\cdot}089$, $\theta = 51°$, the difference was only 0·43 per cent. If in each case, to obviate errors due to any lack of symmetry of setting, the average of the corresponding values on either side of zero is taken, the differences are only 0·45, 1·1 and 0·23 per cent respectively for the three values. The curves show that very approximate constancy of inductance over a more limited range of displacement is

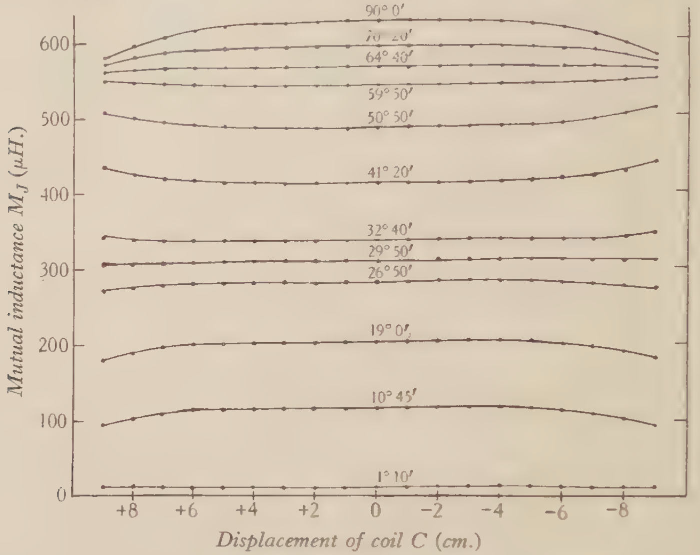

Figure 7. Coils *A* and *B* 16·4 cm. apart, in conjunction. $x^2/a^2 = 0{\cdot}25$. *C* small.

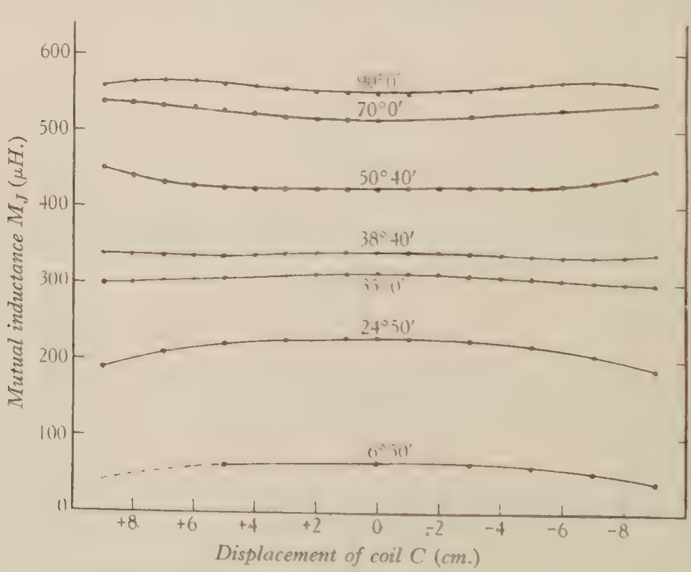

Figure 8. Coils *A* and *B* 19·8 cm. apart, in conjunction. $x^2/a^2 = 0{\cdot}364$. *C* small.

achieved in other positions as a result of a rough balancing out of terms of opposite sign in equation (2) and that the angle for this position gets larger as the separation increases, while a second position of linearity appears after $x^2/a^2 = 0{\cdot}16$ approximately. Theoretical considerations show that θ has risen to $50^\circ\ 46'$ when $x^2/a^2 = 1{\cdot}41$, where a high order of constancy is again achieved. To complete the series, the apparatus was modified so that the rod MN passed through the centre of symmetry of the coil A alone. This corresponds to $x^2/a^2 = 0$, and figure 11 shows, as would be expected, that at this setting linearity is achieved over only a small range.

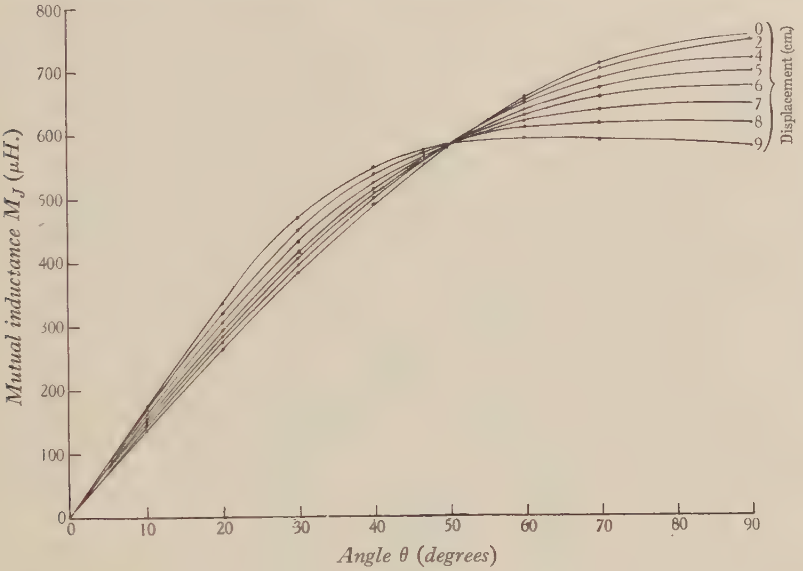

Figure 9. Coils A and B 9·81 cm. apart, in conjunction. $x^2/a^2 = 0{\cdot}089$. C small.

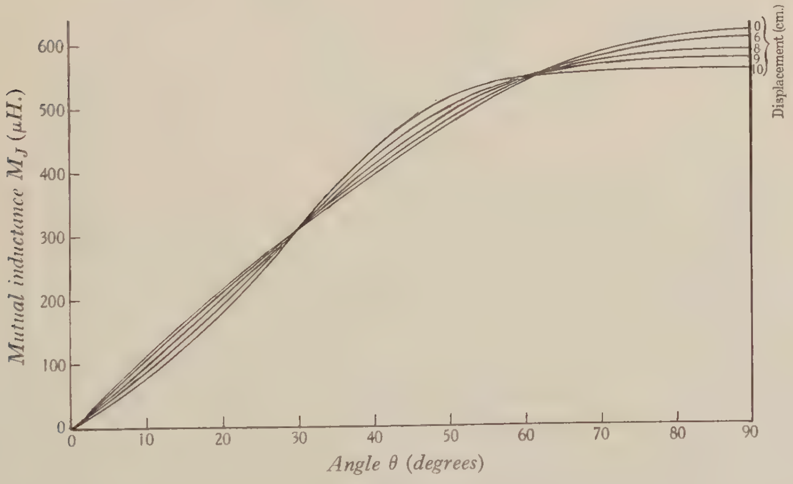

Figure 10. Coils A and B 16·4 cm. apart, in conjunction. $x^2/a^2 = 0{\cdot}25$. C small.

A further series of observations was taken in which the radius of C was not small compared with that of A or B. A coil of 200 turns of average diameter of 7·65 cm. and breadth 1 cm. was used. The separation chosen was that for

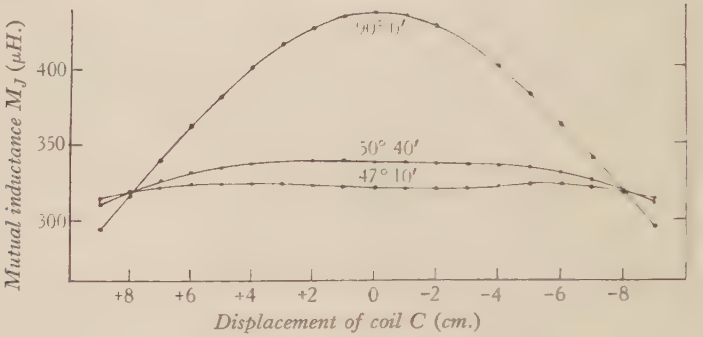

Figure 11. Coil A alone. $x^2/a^2 = 0$. C small.

$x^2/a^2 = 0{\cdot}089$. Figure 12 shows that at about 50°, M_J is constant over a range of ± 7 cm. (A wider range could not be used owing to the presence of the circular framework.) The actual figures show a variation from highest to lowest of 0·44 per cent. This experiment was not done under conditions of perfect symmetry for if the average of readings equidistant from zero be taken the variation is less than 0·1 per cent. It is shown in practice therefore that $M_\theta = GQ \sin\theta$ in such circumstances, even in the case of a large coil. Since, as was indicated in § 1, if a

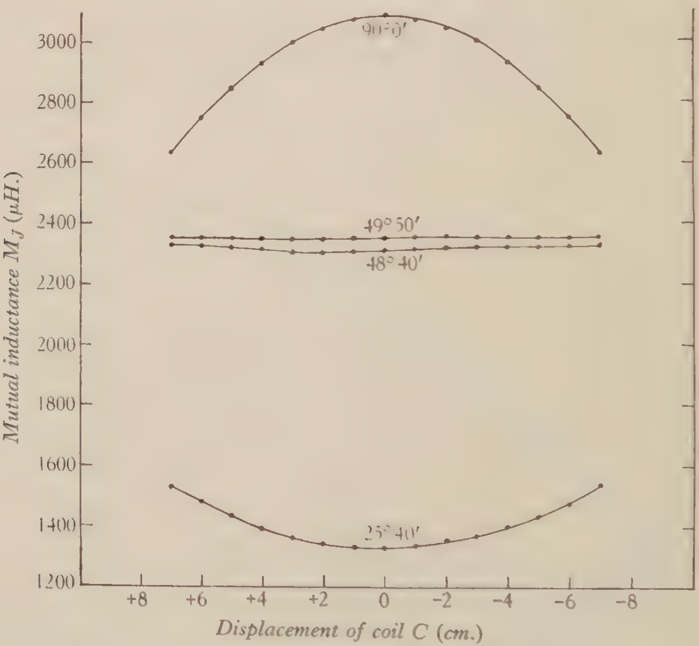

Figure 12. Coils A and B 9·81 cm. apart, in conjunction. $x^2/a^2 = 0{\cdot}089$. C large.

magnet replaces the coil a similar expression is obtained for the flux threading A and B, the breadth and depth of such a magnet will not affect the accuracy of the expression for F in equation (10) so long as the magnet is lying along a line of isomutual inductance.

Measurement of the absolute moment of a magnet. An angle solenoid of length 3·9 cm. and consisting of 467 turns of double-silk-covered copper wire (s.w.g. 24) was inserted in a standard solenoid of known constant G_s, and the mutual inductance M_s between them was found. The solenoid was then mounted as shown in figure 13 on the circular framework previously used, and was so arranged that the centre of symmetry was at O for any angle θ made by its axis with the planes of A and B. This axis was then set to be perpendicular to A and B, the mutual inductance being zero as measured with a.-c. or d.-c., and a magnet was arranged by eye as symmetrically as possible within the solenoid so that its magnetic axis coincided with the axis of the solenoid. The mutual inductance between solenoid and A, B in opposition was then not necessarily zero, owing to the disturbing influence of the magnet, but could be made zero by a slight shift of the magnet. A.-c. was used for the reading since direct currents might shift the magnet and would tend to demagnetize it. If the balance was not sharp in the position of zero inductance, a shift of the magnet along its axis combined with a slight rotation of it was made till the balance was sharp at zero. This indicated that the magnet was coaxial with the solenoid and symmetrically placed with respect to it. The leads to A and B in conjunction were then switched over to a Grassot fluxmeter and the closed circuit containing the angle solenoid was opened. The framework bearing the angle solenoid was swung round through the appropriate angle, according to the separation of A and B, so that the axes of solenoid and magnet lay along a line of isomutual inductance, and the resulting fluxmeter reading F was taken. The magnet was then withdrawn along its axial line till well out of the field of A and B and the fluxmeter reading was taken again. The coils were switched back to the inductometer and M_θ was measured. The average value of F/M_θ for the four sets

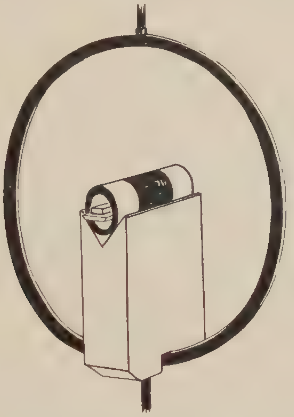

Figure 13.

of readings corresponding to the four possible positions of the magnet was found and when substituted in equation (12) of §·1 gave the absolute moment of the magnet. The values obtained agreed within 1 per cent with values obtained by ordinary laboratory methods, but there was a marked gain in simplicity and the need for corrections for the length, breadth and depth of the magnet was avoided.

§ 3. EXPERIMENTS ON THE MUTUAL INDUCTANCE BETWEEN TWIN COILS IN OPPOSITION AND A SMALLER COIL

The apparatus. This was the apparatus described in the last section but the fields of A and B were in opposition. Figures 14 to 17 for the small coil and figure 18 for the coil of larger diameter show M_P plotted against l for various angles θ. For convenience the distances between A and B were the same as in § 2. For one of these $x^2/a^2 = 0{\cdot}25$, figure 16. Now it is shown in § 1 that if $x^2/a^2 = 0{\cdot}28$ then

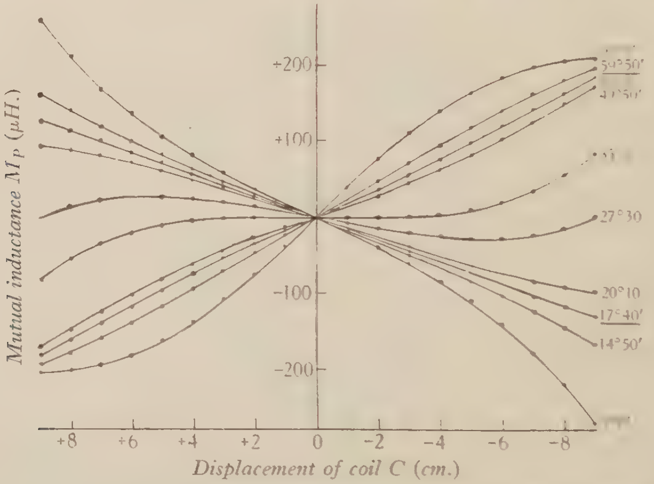

Figure 14. Coils A and B 9·81 cm. apart, in opposition. $x^2/a^2 = 0{\cdot}089$. C small.

M_P/Gq is proportional to l for the angles $\theta = 19^\circ\,53'$ and $\theta = 59^\circ\,27'$. Although A and B were not at the ideal distance apart, the figure shows that straight lines were obtained. Moreover, equation (3) shows that if the second and third terms vanish by choice of θ and x/a respectively, then for the two suitable angles the ratio of the corresponding slopes dM/dl will be equal to $P_2(\sin 19^\circ\,53')/P_2(\sin 59^\circ\,27')$. This works out to be 0·53. The ratio of the two slopes in figure 16 is 0·55 for a value of x/a smaller than it should be.

§ 4. EXPERIMENTS ON THE MUTUAL INDUCTANCE BETWEEN TWIN COILS IN CONJUNCTION AND A LARGE COIL ROTATING BETWEEN THEM

It has been shown* that for the case of two circles A and B arranged as in figure 1, and a coil C rotating about a diameter with its centre at O, where $l = 0$, the mutual inductance M between them can be made proportional to θ to a high order of accuracy. This theory, however, deals with circles, not multi-layered coils and the practical work set out in this paragraph was done with the object of showing that the theoretical constancy of M/θ can be attained with multi-layered coils by arranging a suitable separation of A and B or by varying the radius of C.

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* *Proc. Phys. Soc.* **44**, 200 (1932).

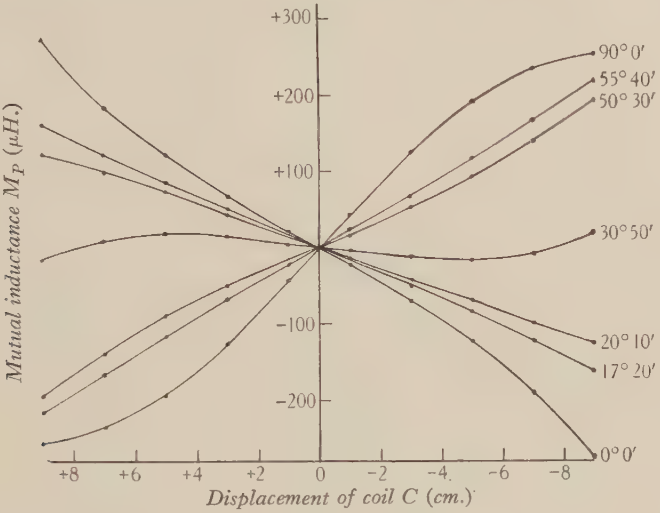

Figure 15. Coils A and B 13·1 cm. apart, in opposition. $x^2/a^2 = 0{\cdot}159$. C small.

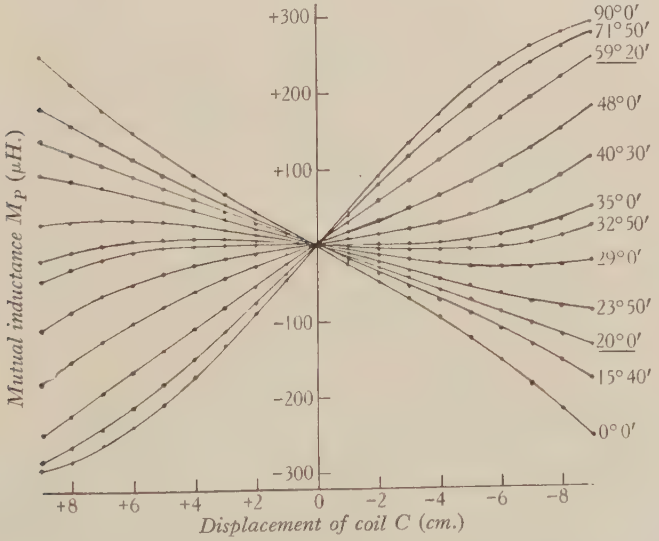

Figure 16. Coils A and B 16·4 cm. apart, in opposition. $x^2/a^2 = 0{\cdot}25$. C small.

The apparatus. The same twin coils A and B were used and were connected in conjunction. A large coil C was wound on a circular wooden former of diameter 18·55 cm. fitting inside an ebonite ring which pivoted on ebonite spindles about a vertical diameter passing through O. The centre of the wooden former was bored so that an angle solenoid *S* consisting of 1360 turns of mean diameter 4·36 cm. could be inserted with its centre of symmetry at *O*, its windings being parallel to those of *C*. The number of turns of *C* was arranged so that the mutual inductances

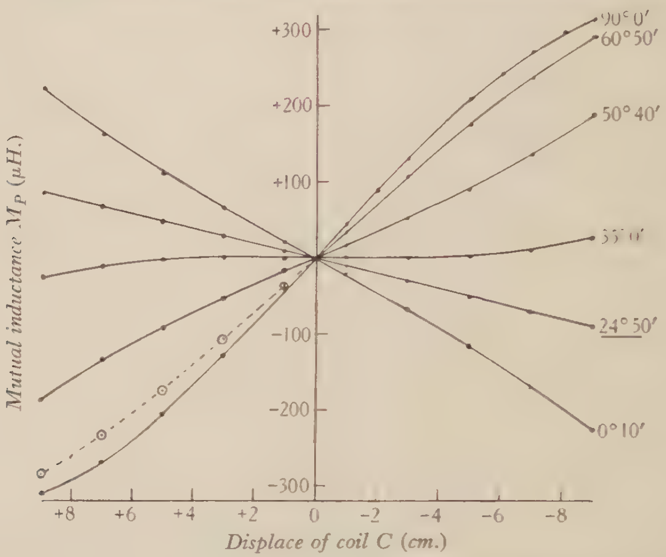

Figure 17. Coils *A* and *B* 19·8 cm. apart, in opposition. $x^2/a^2 = 0{\cdot}364$. *C* small.

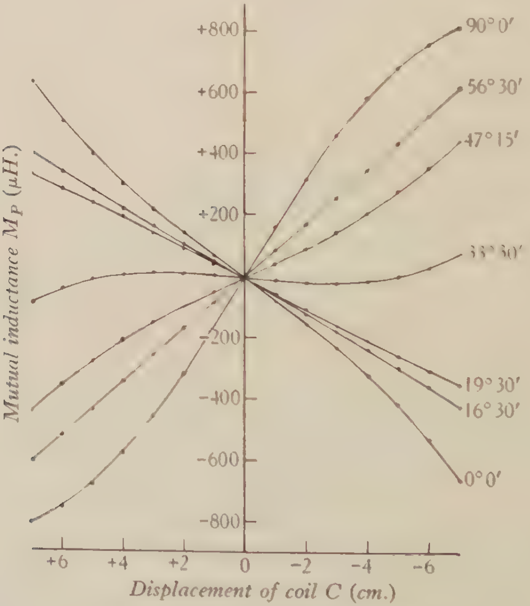

Figure 18. Coils *A* and *B* 9·81 cm. apart, in opposition. $x^2/a^2 = 0{\cdot}089$. *C* large.

between *A*, *B* in conjunction and first *C*, then *S*, always involved the same thousands and the same hundreds studs of the mutual inductometer. In this way errors in the calibration of the inductometer were reduced to negligible proportions.

Method. In the first place, A and B were put as close together as possible and the mutual inductance M between these coils in conjunction and C, on the one hand, and the mutual inductance M_θ between A, B in conjunction and the angle solenoid on the other, were read for the same angle θ, for values between $+ 20°$ and $- 20°$. From M_θ, θ could be calculated and the variation of M with θ determined. It will be seen from column 1 in table 1 that as θ increased M/θ increased. A and B were then separated by about 3·5 cm. more and another set of readings was taken over the same range. Column 2 of table 1 shows that M/θ then decreased as θ increased. The coils were next put in an intermediate position, and column 3 of table 1 shows that in this case M/θ was practically constant. In order to show that proportionality between M and θ could be obtained by altering the radius of C instead of changing the separation of the coils in the first instance, another set of readings was taken for a smaller mean diameter of C. The coils A and B were practically in contact. It will be seen from column 4 of table 1 that M/θ showed a very small but definite decrease when θ increased. It is evident, therefore, that while in this last series the separation of A and B was slightly too large, or the mean radius of C slightly too small, these defects can be adjusted and constancy of the ratio M/θ is attainable in practice to a high degree of accuracy with multi-layered coils over a range of 20° on either side of zero.

Table 1

Approximate range of θ	Value of M/θ when			
	$x^2/a^2 = 0·0367$ $\alpha^2/a^2 = 0·332$	$x^2/a^2 = 0·0893$ $\alpha^2/a^2 = 0·332$	$x^2/a^2 = 0·0613$ $\alpha^2/a^2 = 0·332$	$x^2/a^2 = 0·038$ $\alpha^2/a^2 = 0·31$
0° 30′– 6° 30′	0·03487(5)	0·03348	0·03422	0·03445
1° 50′– 8° 0′	0·03488	0·03348	0·03422	0·03444
3° 20′– 9° 40′	0·03490	0·03347	0·03422	0·03444
4° 50′–11° 10′	0·03491	0·03346	0·03422	0·03444
6° 30′–12° 50′	0·03492	0·03344	0·03421(5)	0·03444
8° 0′–14° 20′	0·03493	0·03342	0·03423	0·03443
9° 40′–16° 10′	0·03494	0·03339	0·03422	0·03442(5)
11° 10′–17° 40′	0·03495	0·03337	0·03422	0·03442
12° 50′–19° 20′	0·03498	0·03335	0·03423	0·03442

§ 5. EXPERIMENTS ON THE USE OF AN ANGLE SOLENOID FOR THE MEASUREMENT OF AN ANGLE

The apparatus. That of the last section was used. Though the coil C was not needed, a slot was cut in its wooden former so that a plane mirror could be fixed with its reflecting surface on the axis of rotation. By means of a telescope and circular scale the angle through which the framework, and hence the angle solenoid, turned could be measured. It was sufficient to show that θ as calculated from $M_\theta/M_{90} = \sin\theta$ was proportional to the scale deflection since this, in its turn, was proportional to the angle in radians. Corresponding readings on either side of zero were (numerically) added to counteract any lack of symmetry of the scale and any uncertainty as to the true zero position due to irreversible inductance. The difference between each reading and the fourth reading below it in order was taken, giving a range of approximately 20 cm. of scale. The maximum error in reading the scale may be taken as between 1 in 1000 and 1 in 2000. Within this degree of accuracy, the angle calculated from M_θ per cm. of the scale is constant, as is shown in table 2.

Table 2

$x^2/a^2 = 0{\cdot}0369$.

Range of readings on scale (cm.)	44–30	40–26	37–23	34–15	30–8	26–3	23–0
Angle (sec.) per cm. of scale	521·3	521·3	521·3	521·4	521·7	522·0	521·0

The radius of curvature of the scale was just under 2 metres. As the range of angle tested in this series was only $5\frac{1}{2}^\circ$ on either side of zero, the calibration was tested over the wider range of $\pm 24^\circ$ of arc. For this, the angle solenoid S was set to give a small mutual inductance with A and B in conjunction and the mirror was arranged to give a scale reading of approximately -25 cm. S was then swung through a deflection corresponding to about 50 cm. of scale and the new inductance was noted. The deflection was such that this was just below 1000 μH. S was then arranged to give just over 1000 μH. and the mirror was arranged to give a reading at approximately -25 cm. again. When the solenoid was swung through an angle corresponding to 50 cm. of scale the inductance was then just under 2000 μH. Another set of readings was taken between 2000 μH. and 3000 μH. Corresponding readings were taken on the other side of zero mutual inductance by a similar method. This system of taking readings reduces errors in the calibration of the inductometer. The maximum error involved in scale estimation is about 1 part in 5000. Table 3 shows the maximum deviation from constant ratio is about the same.

Table 3

$x^2/a^2 = 0{\cdot}0380$.

Angle covered (degrees)	$\frac{1}{2}$–$7\frac{1}{2}$	$8\frac{1}{2}$–$15\frac{1}{2}$	16–24
Angle (sec.) per cm. of scale	523·2	523·2	523·3

These figures show that it is sound in practice to use an angle solenoid to measure angles under 24° on either side of zero. Substitution of the actual values of the dimensions concerned shows that, either with the coils touching ($\psi = 79^\circ$) or in the Helmholtz position, $M_\theta/M_{90} = \sin\theta$ with an error not exceeding 1 part in over 10,000.

Throughout the whole of the practical work described in this paper, therefore, the theoretical expressions established for circles have been shown to apply in practice to multi-layered coils.

§ 6. ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr H. R. Nettleton of Birkbeck College for making the suggestions which led to the work described here, and for the help that he has subsequently given.

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A TECHNIQUE FOR THE PHOTOGRAPHIC DETERMINATION OF THE INTENSITIES OF X-RAY REFLECTIONS FROM POWDERS

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Received July 13, 1934

ABSTRACT. A simple and accurate method of measuring the intensities of X-ray reflections from powders is described. The method consists in reflecting X rays from a plane, stationary layer of powder. Its special advantages are that the absorption factor can be very accurately obtained, and the variation of focusing across the film can be utilized to give lines of approximately the same blackness for reflections of widely different intensities. Three examples are given illustrating the use of the method for comparing reflections from mixed powders, for comparing widely different intensities, and for measuring intensities at large angles of reflection.

§ 1. INTRODUCTION

ALTHOUGH many methods have been used for the photographic recording of X-ray reflections from powders, the majority are more suitable for the measurement of the positions of the reflections than their intensities. For the determination of atomic scattering factors and for related investigations, intensity-measurements are essential and in connexion with such work we have been led to develop a technique which is both simple and accurate. The method is an adaptation of previous methods and utilizes certain features which have usually been regarded more as disadvantages than as advantages.

§ 2. SURVEY OF PREVIOUS WORK

The method most generally adopted is to have the powder in the form of a thin cylinder mounted at the centre of a cylindrical camera. This arrangement is well suited to the determination of the positions of lines, for they are all fairly sharply defined and, within limits, are equally sharp for all angles of reflection. The chief difficulty encountered in measuring intensities by this method is the accurate determination of the absorption factor for a cylindrical specimen. This has been considered by Claassen* and subsequently by Rusterholz†. The absorption factor involves the linear absorption coefficient of the powder in the cylinder and this is difficult to obtain accurately. Furthermore, the comparison of reflections of widely different intensities by this method is not easy, for since all the lines are more or less equally well focused, it is necessary to make the strong lines very black in order to bring out the weak ones; errors are then likely to arise when the blackness of the film measured with a photometer is converted to X-ray intensities by means of a calibration curve.

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* A. Claassen, *Phil. Mag.* **9**, 57 (1930). See also P. Debye and P. Scherrer, *Phys. Z.* **19**, 474 (1918); G. Greenwood, *Phil. Mag.* **3**, 963 (1927).

† A. A. Rusterholz, *Z. f. Phys.* **63**, 1 (1930).

Several methods have been based on the use of a flat layer of powder. If the incident and reflected X-ray beams are equally inclined to the surface of the powder, the expression for the absorption coefficient* is simple and it can be accurately determined. Moreover, the reflected beam is sharply focused, provided the distances from the powder to the film and to the point of divergence of the incident X rays are equal. This method is frequently used in conjunction with the ionization spectrometer because the plate of powder can always be set at the correct angle for each reflected beam, but it is not generally used with photographic recording because many reflections are recorded simultaneously and it is only over a narrow range of angles that there is sharp focusing. This aspect of the matter has been discussed in detail by Brentano† who has designed an X-ray camera which overcomes this drawback by means of a slit moving across the photographic film; the motion of the slit is coupled with that of the powder in such a way that as the powder rotates the lines which are recorded on the film are always sharply focused. In designing this camera, Brentano has been concerned primarily with the measurement of the positions of X-ray reflections and his arrangement is almost equivalent to an ionization spectrometer as regards its focusing properties. In later papers, Brentano‡ shows that this form of camera can also be used for measuring the intensities of reflections and he gives an expression for the absorption factor for X rays reflected from a flat plate.

In our own experiments, a stationary plate method has been finally adopted without the refinements of the Brentano camera. The geometrical simplicity of the method allows the absorption factor to be calculated easily and accurately while the lack of sharp focusing at all points of the film is no disadvantage when intensities alone are required and has actually proved to be a most useful feature of the method.

§ 3. DETAILS OF THE PRESENT METHOD

The camera. A diagram of the camera is given in figure 1. It consists of a stout-walled brass cylinder, 6 cm. in diameter, lined internally with lead. The powder is mounted in a holder attached to a central rod and its position can be read off on a circular scale on the top of the camera. The X-ray beam is collimated by a cylindrical tube, 2 cm. long and 0·7 mm. in diameter, pointing directly at the axis of the camera. The powder is contained in a cavity in a block of mild steel, machined so that its face is accurately plane and lies exactly on the axis of the camera when mounted in position. The cavity is approximately 2·5 cm. long, 1 cm.

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* See A. H. Compton, *X-Rays and Electrons*, chap. v (Macmillan and Co. Ltd., London, 1927).

† J. Brentano, *Proc. Phys. Soc.* 37, 184 (1924).

‡ J. Brentano, *Phil. Mag.* **4**, 620 (1927); **6**, 178 (1928).

wide and 1·5 mm. deep; these dimensions ensure that the whole of the incident beam falls on the face of the powder, that the reflected beams emerge from this face and that for most substances the thickness is effectively infinite. The area of powder irradiated is of the order of 1 to 3 mm.^{2} depending on the setting of the plate with respect to the incident beam. The reflections pass through a horizontal slit in the wall of the camera and fall on a photographic film wrapped round the outside.

Determination of the setting of the powder-holder. The determination of the angle α, figure 1, is important in the calculation of the absorption factor, and an accuracy of 0·2° is necessary for this purpose. A direct X-ray method was found to be sufficiently accurate. By considerably over-exposing the photograph, a sharp edge in the general background is cast by the powder-holder at the point E on the film. Measuring the position of E with respect to the lines on the photograph leads to a direct determination of the angle α. This method is preferable to geometrical or optical methods because it gives the position of the powder-holder with respect to the actual path of the incident X-ray beam.

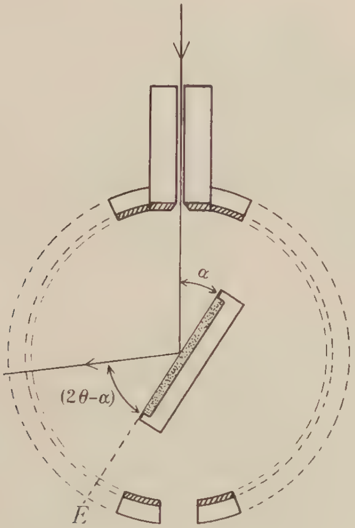

Figure 1. Diagram of the camera.

§ 4. THE INTENSITY OF REFLECTION OF X RAYS FROM POWDERS AND FROM MIXTURES OF POWDERS

The theory of reflection of X rays from crystalline powders has been fully dealt with elsewhere* and it will only be necessary here to adapt the results to the present experimental arrangement. The usual way of obtaining *absolute* values for reflections from powders is to compare the intensities reflected from the substance under investigation with the intensities from a standard substance, usually NaCl,

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* See A. H. Compton, *loc. cit.*

KCl or aluminium, which have already been measured absolutely by other methods*. The two substances are finely powdered and intimately mixed to form a composite plate of powder having an average linear absorption which can be taken to be the same for reflections from the two powders†. A formula will now be developed comparing the intensities I_1 and I_2 of two reflections from powders 1 and 2 respectively.

dI, dV The integrated reflection dI from a small volume dV containing randomly orientated crystals of one kind is given by Compton in the following form:

$$\frac{dI}{I} = \frac{N^2\lambda^3}{2}.\frac{e^4}{m^2c^4}.F^2.\left(\frac{1+\cos^2 2\theta}{\sin 2\theta}\right).\frac{pl}{8\pi\, Sr.\sin\theta}.dV \qquad \text{......(1)},$$

where

I I is the intensity of the incident beam;

S S the area of the incident beam;

r r the distance of the film from the crystal holder;

l l the length of the line recorded on the film;

p p the multiplicity factor for the reflection;

N N the number of unit cells per unit volume of the crystal‡;

F F the amplitude scattered per unit cell in terms of the amplitude scattered by a single electron;

c, m, θ and λ, e, c, m, θ have their usual significations.

When reflection takes place from a plate of powder, the effective volume element

ρ' becomes $dV(\rho'/\rho)$, where ρ' is the effective density of the substance in the plate

ρ and ρ is the true density of the substance itself. With the present experimental arrangement it is convenient to take for the volume element, the powder irradiated lying between depths x and $(x+dx)$. It may then easily be shown that

$$dV = \frac{S.dx}{\sin\alpha}.\frac{\rho'}{\rho} \qquad \text{......(2)},$$

α where α is the angle between the incident beam and the surface of the powder, figure 1. Combining equations (1) and (2) and grouping all the constant terms together, we have

$$dI = (\text{constant}).p.N^2.F^2\left(\frac{1+\cos^2 2\theta}{\sin\theta.\sin 2\theta}\right)\frac{\rho'}{\rho}.\frac{dx}{\sin\alpha}.$$

I_r The total reflected intensity, I_r, is obtained by integrating this equation from $x=0$ to $x=\infty$, and taking into account the absorption of the incident and reflected X rays for each layer dx. A little consideration shows that for a layer of powder at a depth x the incident rays traverse a distance, $x/\sin\alpha$ and the reflected rays a distance $x/\sin(2\theta-\alpha)$ in the powder, so that the total distance in the powder is

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* R. W. James and E. M. Firth, *Proc. R.S.* A **117**, 62 (1927); R. W. James and G. W. Brindley, *Proc. R.S.* A **121**, 155 (1928); R. W. James, G. W. Brindley and R. G. Wood, *Proc. R.S.* A **125**, 401 (1929).

† The conditions under which this holds are discussed in § 5.

‡ Compton obtained equation (1) by considering a simple cubic lattice containing atoms of only one kind. In extending this result to crystals of other kinds, N and F apply to the *unit cell* of the structure and have the definitions given above. This point has often been overlooked in carrying over Compton's notation to the general case.

$$\{x/\sin\alpha + x/\sin(2\theta-\alpha)\}.$$

The total intensity reflected from the block of powder is therefore given by

$$I_r = (\text{constant}) \times \frac{pN^2F^2}{\sin\alpha}\left(\frac{1+\cos^2 2\theta}{\sin\theta\sin 2\theta}\right)\frac{\rho'}{\rho}\int_{x=0}^{x=\infty} e^{-\mu'\{x/\sin\alpha + x/\sin(2\theta-\alpha)\}}.dx,$$

where μ' is the coefficient of linear absorption for the powder. Evaluating the integral, we have finally μ'

$$I_r = (\text{constant})\, pN^2F^2\left(\frac{1+\cos^2 2\theta}{\sin\theta.\sin 2\theta}\right)\frac{\rho'}{\mu'\rho}\left[\frac{\sin(2\theta-\alpha)}{\sin(2\theta-\alpha)+\sin\alpha}\right].$$

The expression in the square brackets is the absorption factor for a plate which is effectively of infinite thickness, and its value is independent of the actual value of μ'. This is an important advantage of the plate method as compared with the cylindrical-rod method, because in comparing the intensities of two reflections from a plate it is not necessary to know the linear absorption of the powder. The last equation may be written more conveniently as follows:

$$I_r = (\text{constant}).p.N^2.F^2.\phi(\theta).A.\rho'/\rho \qquad \text{......(3)},$$

where $\phi(\theta)$ includes all the trigonometrical functions and A is the absorption factor. This expression for A is essentially the same as that given by Brentano*. ϕ, A

When *relative* values of F for a single substance are required, equation (3) reduces to the following simple form:

$$I_r = (\text{constant}).p.F^2.\phi(\theta).A \qquad \text{......(4)}.$$

When a mixture of two powders is considered†, the form of equation (3) may be modified in the following way. The effective density ρ' is proportional to G, the weight of the reflecting substance present in the mixture. The true density ρ can be written as $M.m_H/a^3$, where M is the total molecular weight of the unit cell, M
m_H is the mass of the hydrogen atom, and a^3 is the volume of the unit cell if the m_H, a
latter is assumed to be cubic; otherwise, the correct expression for the volume of the cell must be used in place of a^3. Also, $N=1/a^3$. Substituting these results with the appropriate suffixes in equation (3), we obtain finally

$$\frac{I_1}{I_2} = \frac{p_1.F_1^2.\phi_1(\theta).A_1.G_1}{p_2.F_2^2.\phi_2(\theta).A_2.G_2}\left(\frac{a_2}{a_1}\right)^3\frac{M_2}{M_1} \qquad \text{......(5)}.$$

In this equation (I_1/I_2) is the ratio of the intensities of two reflections as measured by the method described above. If F_1 is the amplitude reflected by a unit cell of F_1
the standard substance, NaCl, KCl, or Al, then the equation can be used to measure F_2, the amplitude reflected by a unit cell of the substance being investigated. F_2

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* *Loc. cit.*

† For an intimate mixture of two powders, a common value of μ' may be assumed.

§ 5. THE PREPARATION OF SATISFACTORY BLOCKS OF POWDER

In our experiments we have sometimes found it surprisingly difficult to obtain really satisfactory blocks of powder. Before equations (4) and (5) can be applied it is essential to ascertain whether the conditions postulated in deriving equation (1) are satisfied, viz., that the powder consists of a random arrangement of very fine particles.

Difficulties may arise in several ways in obtaining a random distribution of the particles. If the particles are flat or elongated or of a flaky nature they are almost certain to have a preferential orientation in the powder; we have found that this happens with commercial aluminium powder and the intensities obtained from such a powder are not in the same ratio as if the particles were randomly distributed. If the lines of the X-ray photographs show any trace of individual spots and are not continuously black, then the particles are evidently so large that reflection occurs only along certain directions depending on the way in which the individual particles are arranged. Photographic methods have an important advantage here over ionization methods, because spottiness of the lines might very easily be overlooked in the latter method.

The maximum particle-size which can be tolerated in a powder depends on the substance and on the radiation. Quite roughly one may say that at least half the radiation falling on a particle must pass through it in order that a sufficient number of particles may be irradiated. Assuming the usual equation for X-ray absorption, $I = I_0 e^{-\mu x}$, where I is the intensity transmitted through a thickness x, μ is the linear absorption coefficient and I_0 is the incident intensity, and taking I/I_0 to be not less than $\frac{1}{2}$, we have that x must be not greater than (log. 2) μ, i.e., x must be less than 0·7 μ approximately. In the case of copper K_α radiation reflected from aluminium and from copper, the particle-sizes must be less than about 50×10^{-4} cm. and 15×10^{-4} cm. respectively. In this example the radiation will penetrate effectively four or five layers of particles and if 1 mm^2 of the powder surface is irradiated about 2000 aluminium particles or about 10,000 copper particles will contribute to the reflection. In this connexion it may be mentioned that the plate method is superior to the cylindrical-rod method in that it allows a much larger volume of powder to be irradiated; more particles take part in the reflection and it is therefore easier to satisfy the requirement that the particles shall be randomly distributed.

I

I_0

The preparation of sufficiently fine particles sometimes presents difficulty and no general rules can be given. But it may be well to point out that in the case of metals and alloys, where the usual practice is to obtain the powder by filing and sieving through a fine-meshed gauze, the process of filing may affect the intensities of reflection as a result of distortions produced in the metal; we shall discuss this in detail elsewhere. In the case of potassium chloride we have found that repeated grinding by hand in a mortar will not give sufficiently fine particles; in such a case chemical methods may be used.

In comparing reflections from mixed powders, even greater care must be taken to obtain suitable particles. If the sizes and absorption coefficients of the two kinds of particles are approximately the same, then the equations in § 4 are applicable, but when these conditions are not satisfied the question of the absorption in a composite block of powder must be considered in more detail. In such a case, an average absorption coefficient for the whole powder cannot be assumed and allowance must be made for the distribution of the two kinds of particles. This has been carefully worked out by Schäfer* for the case of copper K_α radiation reflected from a mixture of aluminium and iron for which the linear absorption coefficients are respectively 130 and 2600. In this somewhat extreme case the equations in § 4 are only applicable if the particle-size is of the order of 10^{-5} cm.

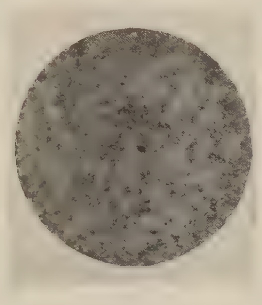

Figure 2. Microphotograph of Cu-KCl mixture. (Magnification 80 diameters.)

It is not always easy to prepare a satisfactory mixture of two constituents. Metals, such as aluminium and copper, mix readily but a metal and a powder such as potassium chloride are more difficult to mix. In the latter case the process is facilitated by adding a small quantity of alcohol and stirring continually while the alcohol evaporates; when the mixture becomes pasty it is transferred to the powder-holder and the surface is smoothed quite flat with a glass plate. When the mixture is dry, a perfectly smooth surface is obtained which does not crack. Figure 2 shows a microphotograph of a Cu-KCl mixture obtained in this way.

§ 6. THE ABSORPTION FACTOR AND THE QUESTION OF FOCUSING THE REFLECTED BEAMS

The absorption factor A has been shown to be given by the equation

$$A = \left[\frac{\sin(2\theta - \alpha)}{\sin(2\theta - \alpha) + \sin\alpha}\right] \qquad \text{......(6).}$$

If the plate is set so that the incident and reflected beams make equal angles with the surface of the powder, then $\theta = \alpha$ and the expression for A reduces to $\frac{1}{2}$; substituting this special value of A in equation (3) we have the usual expression for the intensity of reflection from a powder as it is generally measured with an ionization spectrometer. Furthermore, if the distances from the powder to the film and to the source of X rays are equal, then the condition $\theta = \alpha$ is also the condition for sharp focusing of the reflected beam.

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* K. Schäfer, *Z. f. Phys.* **86**, 738 (1933).

It is most important in using the present method to have a clear picture of how the absorption factor and the focusing effect are related and of their bearing on the shape and intensity of the lines recorded on the photographic film. Suppose that, as often occurs in practice, we wish to compare two reflections, a strong reflection a at a small angle θ_a and a comparatively weak reflection b at a larger angle θ_b. If the powder plate is set so as to focus b sharply, then α must be made approximately equal to θ_b and A_b will be about 0·5. Under these conditions the strong reflection a will be much less sharply focused than b, and A_a will be less than A_b and may be about 0·2 or 0·3. Thus, by choosing the geometrical conditions rightly, the strong reflection can be reduced by absorption and can be broadened by the absence of sharp focusing, with the result that the lines a and b recorded on the photographic film may both be approximately of the same blackness. It is not at all essential when intensities are being measured that the lines should be sharply or equally focused; it is very much more important that they should be of about the same degree of blackness, so that the maximum accuracy can be obtained when the film is photometered. The variation of focusing produced by a stationary plate has hitherto been regarded as a disadvantage, and it is a disadvantage when the positions of lines are required accurately, but when intensities are required it is definitely an advantage.

In practice it is very useful to have a large-scale diagram of A plotted against θ for a series of values of α changing by 5° at a time; a graph of this kind is shown in figure 3. In using the diagram it should be remembered that the horizontal line through $A = 0·5$ corresponds to $\theta = \alpha$ which is the condition for sharp focusing.

When reflections from a mixture of two powders are to be compared, the method is particularly adaptable, for there are three factors by which the photographic densities of the lines can be controlled, viz., the composition of the mixture, the absorption factor, and the focusing-effect.

§ 7. PHOTOGRAPHY AND PHOTOMETRY

To secure uniform development, the films were mounted vertically in the developer and were kept in motion by a simple mechanical arrangement. They were calibrated directly in terms of X-ray intensities by means of a step wedge in the manner described by Bouwers*. It has previously been shown† that the density is directly proportional to the X-ray intensity up to a certain point depending on the nature of the film; this limit is at a density about 1·0 above the unexposed part of the film for the Agfa-Laue films used in our experiments. It is usually possible to keep the densities of the lines below this limit so that the calibration curve connecting intensity with photographic density need not be used in obtaining

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* A. Bouwers, *Physica*, **3**, 113 (1923).

† G. W. Brindley and F. W. Spiers, *Phil. Mag.* **16**, 686 (1933). References to earlier work will be found in this paper.

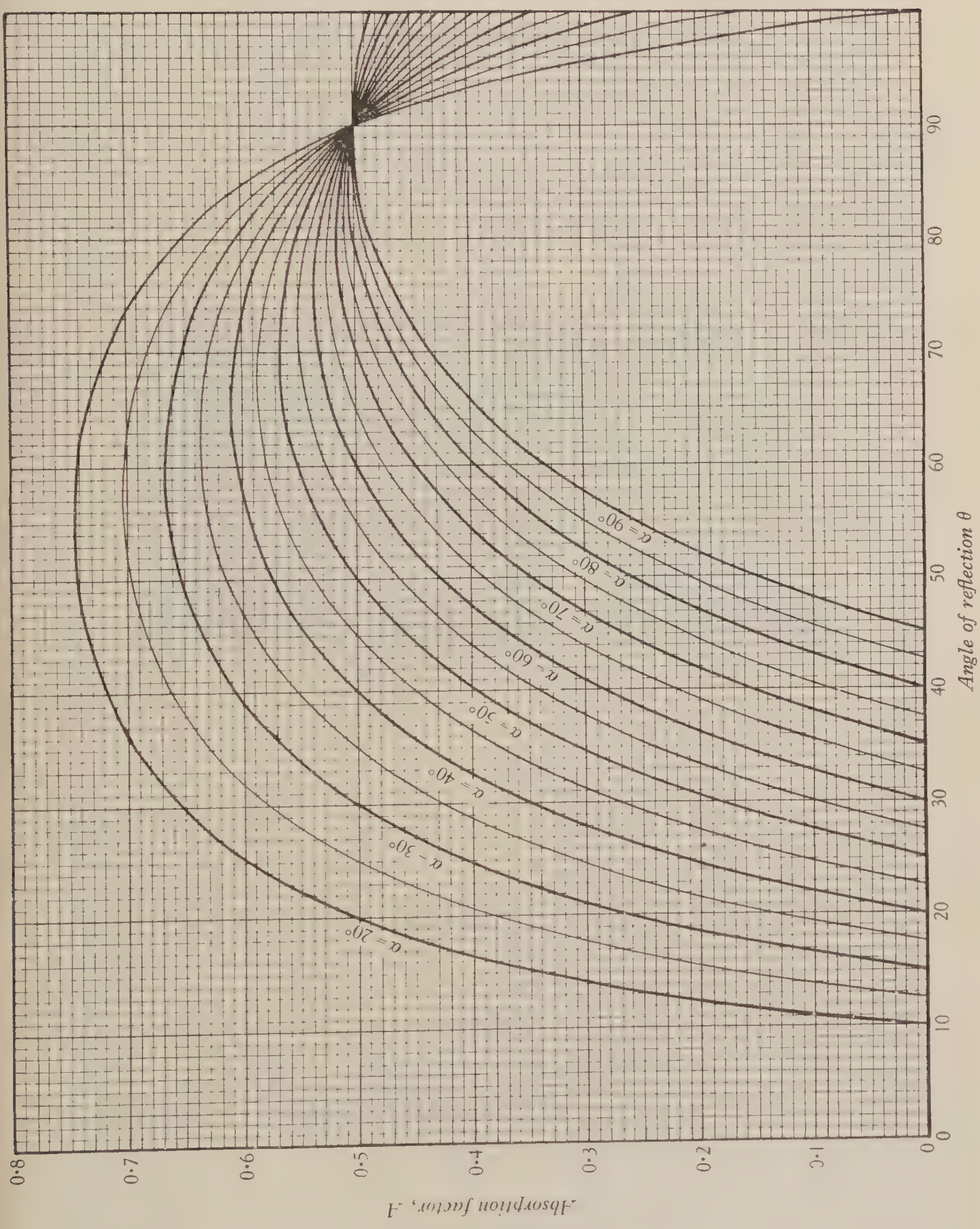

Figure 3. The absorption factor A plotted as a function of θ and α.

relative intensities; it is, however, a useful safeguard to have this calibration wedge on every film.

The films are most satisfactorily photometered by a null method which determines the densities directly in terms of a calibrated photographic wedge. The lines are then plotted out on squared paper and the areas above the general background taken as measures of the integrated reflections. Background variation due to the grain-size of the film is the chief source of error in determining these areas. For lines of medium intensity the error is quite small but becomes a serious matter for very weak reflections. Hence it is advantageous to have a method by which the energy of a weak reflection can be concentrated into a narrow line standing well above the background. Figure 4 shows two reflections from a mixture of copper and aluminium taken with a Cambridge recording micro-photometer*; the two reflections are Cu (220) and Al (311). The background variations shown in this figure are typical of a rather coarse-grained X-ray film; finer-grained films give slightly smaller variations, but the increase in accuracy is small and in general does not justify the much longer exposures which are necessary.

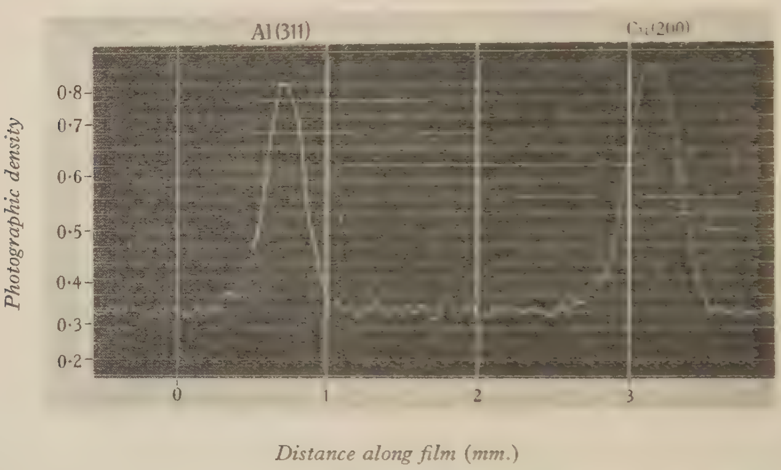

Figure 4. Microphotometer trace of Cu (220) and Al (311) reflections from mixed copper and aluminium powders.

§ 8. TYPICAL RESULTS

Finally we shall give three examples to show how the method works in actual practice.

Example (1). Table 1 illustrates the use of the method in comparing reflections of widely different intensities from a single substance.

The figures in the last two columns of Table 1 show that although the values of $pF^2.\phi(\theta)$ for these three reflections are approximately in the ratio 5 : 2 : 1, the actual intensities which have to be measured are almost equal as a result of choosing

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[*] This instrument was purchased out of a grant made to Prof. Whiddington by the Royal Society.

an appropriate value for α. Moreover, the very strong (111) reflection is not focused so well as the (220) reflection and, as a result of this, the photographic densities for these reflections are practically equal.

Table 1. Data for the intensity of reflection of copper Kα radiation from copper powder

Reflection	2θ	α	$(2\theta - \alpha)$	A	Relative intensities from films $pF^2.\phi(\theta).A$	Relative values of $pF^2.\phi(\theta)$
(111)	43° 20′	37° 18′	6° 2′	0·148	141_8	474
(200)	50° 28′	,,	13° 10′	0·273	106_0	193
(220)	74° 8′	,,	16° 50′	0·497	*100*	*100*

Example (2). Table 2 shows the accuracy with which reflections from mixed powders can be measured.

Table 2. Comparison of KCl (420) and KCl (422) + Cu (220) for copper Kα radiation

Film ...	660*a*	660*b*	661*a*	661*b*	662*a*	662*b*	663*a*	663*b*	
KCl (420)	678	601	808	680	641	581	670	838	Areas
KCl (422) + Cu (220)	1220	1135	1475	1246	1231	1118	1282	1556	
KCl (420)	100	100	100	100	100	100	100	100	Relative intensities
KCl (422) + Cu (220)	180	189	183	183	192	192	191	186	

Average results: KCl (420) = 100
KCl (422) + Cu (220) = 187

These results show the order of accuracy which is obtainable in measuring relative intensities photographically. The variation of the individual values about the mean value is due partly to inhomogeneities in the films themselves and partly to small uncertainties arising from the grain-size of the films. Complete agreement between the results from a series of films cannot be expected, but when an average is taken of the results yielded by six or eight films the error is not likely to be large in the final result; the results given in the next example support this statement.

Example (3). Table 3 shows the accuracy which can be obtained at large angles of reflection, where the increase of general scattering makes the determinations much more difficult than at small angles of reflection.

In the first part of table 3 we give the necessary data for calculating the relative values of $pF^2.\phi(\theta).A$ for four reflections of copper Kα radiation from aluminium powder. The F values used were interpolated from those obtained by James, Brindley and Wood* for a large single crystal of aluminium. The second part of the table gives the relative intensities measured from 14 films. The probable error in the last column was obtained as follows. If r is the difference between an actual value and the mean value, then the probable error is taken as $\surd(\Sigma r^2)/n$, where n is the number of observations*. The agreement between the observed and the calculated values is very satisfactory and shows that the present method of measuring intensities is reliable provided that the average of a sufficient number of films be taken.

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* *Loc. cit.*

Table 3. Data for the intensity of reflection of copper Kα radiation from aluminium powder

(1) Calculated values of relative intensities from equation (4)

Reflection	2θ	α	$(2\theta - \alpha)$	A	p	F^2 (James and Brindley)	$\phi(\theta)$	$pF^2 . \phi(\theta) . A$ (relative values)
(311)	78° 22′	61° 24′	16° 58′	0·249	24	33·5	1·683	118·1
(331)	112° 10′	—	50° 46′	0·468	24	17·1	1·486	*100·0*
(420)	116° 46′	—	55° 22′	0·484	24	16·0	1·582	102·8
(422)	137° 44′	—	76° 20′	0·525	24	$11{\cdot}5_6$	2·467	125·8

(2) Observed values of relative intensities

Reflection	Observed relative intensities. Mean values for 14 films	R.m.s. error
(311)	118_5	± 1_0
(331)	*100*	± 0
(420)	104_0	± 1_0
(422)	126_0	± 1_5

This last example is a fairly stiff test of the method because it involves reflections over a wide range of angles, from 78° to 137°, a wide range of absorption factors, and a fairly large variation in the degree of focusing. The angle α was chosen to be about 60° so as to obtain good focusing for the (420) and (422) reflections; these are more difficult to measure owing to the partial resolution of the Kα_1 and Kα_2 lines. The (311) reflection is much stronger than the others because of the much larger value of F^2, but it was cut down by the absorption factor and by broad focusing, so that it appeared on the films with about the same degree of blackness as the other lines.

§ 9. ACKNOWLEDGMENTS

Finally we wish to thank Professor Whiddington for his interest in these experiments and the Government Grant Committee of the Royal Society for a grant with which some of the necessary apparatus was bought.

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* See A. S. Eddington, *Proc. Phys. Soc.* **45**, 271 (1933).

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A SELF-SYNCHRONIZED SYSTEM FOR IONOSPHERIC INVESTIGATION BY THE PULSE METHOD

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Communicated by Prof. E. V. Appleton, F.R.S., April 7, 1934.

ABSTRACT. The paper describes an arrangement for the convenient study of the ionosphere by the pulse method when the sending and receiving stations are of necessity in different locations having no interconnection (e.g. no common mains supply) to provide a synchronizing-frequency.

Even under conditions of considerable electrical interference, the system provides (*a*) an extremely steady pattern of layer-height and echo-intensity on the cathode-ray oscillograph screen, suitable for visual observation or for photographic snapshot records; (*b*) immediate photographic delineation of a curve showing the variation of layer-height with frequency; and (*c*) continuous records of the variation of layer-height with time. It has the advantage that local disturbances connected with the mains supply do not produce a stationary pattern on the screen, as is the case when the pulse-recurrence frequency is the same as that of the mains supply at the receiver.

A very simple and positive method of modulating a pulse transmitter, which uses a thyratron alone without the usual amplifying or auxiliary control valves, is described.

A further innovation is that the calibration of the time base or scale of equivalent height is impressed permanently on the record, thus providing a continuous check of scale value, and facilitating the interpretation of the records.

§ 1. THE GENERAL PROBLEM

In the usual application of the group-retardation method of Breit and Tuve(1) for the investigation of the ionosphere, successive pulses of radio-frequency energy are radiated at regular intervals and (after suitable treatment at the receiver) are exhibited, together with any echoes which may be reflected from the upper atmosphere, on a cathode-ray oscillograph or similar device. This delineation at the receiver is usually accomplished by using a time base whose recurrence frequency can be kept the same as that of the received pulses. The pulses cause deflections of the oscillograph spot at right angles to the sweep of the time base, and since the echo is delayed with respect to the ground pulse it is relatively displaced on the time base, giving the now familiar echo pattern. If any exhaustive study is to be made of the heights of return and the intensities of the echoes, this pattern should remain extremely steady over long periods and under varying conditions quite automatically, otherwise the labour of manipulation becomes excessive.

Consider the steadiness in position required for the different types of records taken in these investigations. For snapshot work, the time during which the pattern

P', f

should remain stationary need be no longer than $\frac{1}{5}$ sec., though, where the general noise is considerable, much better discrimination can be obtained by exposures of 1 sec. or more. Provided that the frequency and phase of occurrence of the pulse are reasonably steady this presents little difficulty, for the frequency of recurrence of the time base can be made equally steady. For P', f curves, showing the relation between the equivalent path P' and the frequency f, where the time spent on each frequency must be reduced to a minimum to obviate variations of height with time, the main requirements are that the pattern shall take up its position as soon as possible and that it shall remain stationary long enough to be photographed. Further, since one snapshot cannot be regarded as a fair sample of the conditions for that frequency, several such pictures, or their equivalent, are required. This entails constancy in position over a period of some 15 sec., and to attain this we must have considerable stability in both the pulse and time base recurrence-frequencies, together with rapidity of phase adjustment or, better still, automatic phase adjustment.

t

For P', t curves, i.e. curves showing the variation of the equivalent path with time, conditions are much more stringent. The pattern must remain in the field of the camera indefinitely, and any unavoidable variation in position must be small and gradual. The amount of variation which can be allowed depends mainly on one's personal idea of a good record, but it should at most be less than one-fifth of the distance between the ground pulse and the first echo. Thus there must be not only frequency stability in the two recurrence-frequencies but also accurate phase-control, for the relative phase must not vary by more than a degree or two.

Consider now the influence of local conditions at the transmitter and receiver. When a suitable common frequency is already available at both, the problem almost resolves itself. The simplest arrangement is that in which the same a.-c. mains supply is available and the network constituting the interconnexion is simple and direct. All that is then necessary is to ensure that the phase of occurrence of the pulse and the phase of commencement of the time base, relative to the mains supply, should be constant, for the phase of this supply at sender and receiver will necessarily be almost identical. If, however, the two stations are interconnected by the mains supply, but through a major portion of the network, particularly through a number of generating stations, the phase of the supply at the two points is likely to differ considerably, according to the distribution of the load between the various generating stations.

No other common frequency suggests itself, but there is the possibility of providing one either by landline or by a separate radio channel. However, as we already have at the receiver such a common frequency in the form of the pulse, an additional source of common frequency should be unnecessary.

When a common mains supply is not available, the problem can be subdivided into the cases where the supply at the transmitter is a.-c. and where it is not; the nature of the supply at the receiver is not usually a factor to be considered. When a.-c. is available, the transmitting apparatus is simpler and more economical if the frequency of the supply is used as the recurrence-frequency of the pulse, and thus the stability of this recurrence-frequency is at once fixed. The stability is likely to be rather poor, especially on mains supplies which do not guarantee a service for electric clocks.

The use of a stable oscillator at the receiver to control the time-base recurrence-frequency is then out of the question and something more flexible which will follow any short-period variations must be provided. This is essentially the province of a self-synchronized arrangement.

Where d.-c. power only is available at the transmitter, a local oscillator must be provided to control the recurrence-frequency of the pulse. One might use either accurately controlled oscillators at both stations with only a small amount of locking to maintain exact synchronism, or use simple control oscillators with accurate and positive locking. The former would be expensive and inflexible and it will be shown to have no particular advantage.

§ 2. THE PARTICULAR PROBLEM

A statement of the conditions for which the system was designed will assist in following the lines of development. The transmitter is located at King's College, Strand, and the receiver at the Halley Stewart Laboratory, Hampstead; the distance between the two is about 7 km. It was necessary to take continuous records of layer-height and also to make rapid determinations of the equivalent height at closely spaced frequencies; in fact as near an approach as possible to a continuous P', f curve was desired.

Both a.-c. and d.-c. power were available at the transmitter, and at the receiver there was also a.-c., but it differed in frequency from that at the transmitter and from that at the National Physical Laboratory, Teddington, the transmissions from which are much used also. Another source of trouble was the electrical interference from domestic appliances in the neighbourhood. The two disadvantages offset each other to some extent, for the disturbances do not give a stationary pattern superimposed on the echo pattern. Where such disturbances are troublesome, it is a very definite advantage if the pulse-recurrence frequency differs from that of the mains supply at the receiver.

§ 3. THE TRANSMITTING SYSTEM

The transmitter was originally operated from the d.-c. power supply, but the strength at the receiver was found to be insufficient to operate any self-synchronized scheme, so it was decided to utilize the transmitting valves (Mullard SW2B) at the voltage limit, since the dissipation is low with pulse transmissions, and at the same time to simplify the apparatus by operating entirely from the a.-c. mains. A transmitter for d.-c. operation will therefore be described, and the necessary modifications when a.-c. is to be used will be indicated.

The aerial presents the first problem since the transmitter is located on the roof of King's College and the earth below is very vague; a horizontal dipole probably offers the best solution. Much trouble might be saved by the use of a number of aerials of different lengths connected in parallel, a plan adopted by workers in America(2), for the coupling of the aerial to the oscillator then presents much less difficulty. Because of the wide variation of the impedance presented by the aerial for different frequencies, it is hopeless to expect reasonable efficiency from a fixed coupling, even for the range covered by one coil, unless, perhaps, a separate aerial is used for each coil. Moreover, the whole range of frequencies from 2 to 10 Mc./sec. was to be covered without a coil-change, by the use of a variometer. Variable coupling was therefore essential and capacitive coupling was the most convenient, since it can be continuously variable; such coupling also reduces the radiation of harmonics. Closely allied to this question of coupling-efficiency is that of the dependence of the length of the pulse on the load introduced into the oscillatory circuit from the aerial. If the loading is light, the time of decay of the oscillations may well be as long as 0·2 millisecond, giving a long and inefficient pulse particularly unsuitable for schemes where the transmitter and receiver are very close to each other. The aerial therefore should always be coupled as closely as possible to the oscillator, up to the point where the rate of build-up of the oscillations balances the rate of decay.

The step-down ratio required (from 25,000 to 100 Ω.) requires a large-output condenser, but an ordinary Cyldon receiving condenser of 0·001 μF., when immersed in good transformer oil, gave the requisite capacity and withstood the radio-frequency voltages across it. This condenser is shown at C_2 figure 3. The tuning condenser C_1 is centre-pointed, with 0·0003 μF. on each side, and of the Cyldon small transmitter type.

To obviate plug-in coils, the variometer L_1 was constructed and this, in conjunction with the continuously variable output coupling used, permitted the frequency range from 2 to 9 Mc. sec. to be covered without discontinuity. Trouble was encountered in the construction of the variometer owing to the voltage step-up across either stator or rotor relative to that across the whole variometer in the minimum position. This step-up can easily be 5 to 1, and since the variometer is balanced, the stress in the insulation at the two lead-in connexions to the rotor is very high. Steatite, however, was found to be suitable as an insulating material and is easily worked.

The two halves of the tuning-condenser and the variometer are ganged but the output coupling condenser could only be included in the ganging by cutting a special cam. Shunt feed, constituted by L_2, C_4, is adopted for the anode supply, in order to keep dangerous voltages away from the controls and to give only radio-frequency voltages across the tuning-condensers, which are already working close to the voltage limit. The space-wound feed choke gave no trouble due to resonance effects anywhere in the frequency range. When the anode supply is alternating almost the full anode voltage comes across the tuning-condensers because the output circuit is not earthed in any way, so that it is necessary to provide two resistances R_2 of about 10,000 Ω. connecting the two sides of the output circuit to earth.

With a continuous-wave oscillator the feed-back is determined in accordance with a compromise between efficiency and power output, but for a pulse transmitter we are concerned at this point rather with the requirement of maximum power and rate of build-up of the oscillations. For this we require considerable feed-back and it is provided by a fixed condenser C_3 of 0·0001 μF. Resistances R_4 of 10 Ω. connected directly in series with the grids serve to damp out spurious oscillations.

Mechanically interlocked switches S_1, S_2, S_3 ensure that filament, bias and anode voltages are applied in their proper order, and appropriate meters and regulating resistances are provided. A thermo-ammeter measures the current flowing in the aerial, and a switch permits the use of a 40-metre dipole or half of it as required. This switching is also effective in unbalancing the dipole sufficiently to give adequate strength to the ground ray at the receiver.

When the anode supply is alternating, it is necessary to have a capacity C_7 of about 0·1 μF. across the secondary of the high-tension transformer T_3 to give the necessary steep slope to the pulse of current for the valves. This constitutes a considerable wattless load and should be balanced by a choke preferably connected across the primary of the transformer. The choke is also necessary to ensure that the phase of the anode voltage shall be independent of its amplitude.

§4. THE MODULATING SYSTEM

Pulse modulating systems have appeared in considerable number(3), from the simple squegger oscillator to master-oscillator types in which modulation is effected in the amplifying valve. The criticism levelled at the simple oscillator, that the band of frequencies is excessive and erratic, does not seem to be justified in fact, and in any case with pulses of the requisite short duration the frequency band to which the measurements are to be referred is limited more by the receiver than by the transmitter. Tests at the receiver have shown that any frequency-modulation which may be present is insufficient to cause a phase-shift of the carrier of 10° in the duration of the pulse. The use of the master oscillator, then, is not justified, except for certain special investigations, in view of the accompanying expense and loss of flexibility. Another criticism of the self-excited transmitter is that it cannot easily be modulated with certainty on the grid, but the circuit to be described achieves this result positively and it is quite simple.

The value of the bias necessary to quench oscillations which have been initiated may be as high as one-quarter of the anode voltage, particularly when the drive is made very heavy to give a rapid rate of build-up. The small commercial thyratrons are rated at 1000 volts peak, forward and inverse, and since nearly twice this value can be obtained for bias purposes without exceeding the limit quoted it should be feasible to use such a thyratron for direct grid modulation for powers up to about 1 kW.

Consider the simple circuit of figure 1 (*a*), consisting of a choke *L*, a condenser *C* and a thyratron *T* connected in series across a supply circuit. Suppose the condenser to be initially uncharged and the thyratron in the non-conducting state. Then if the thyratron is tripped the condenser charges to twice the voltage of the supply, for the low resistance of the thyratron permits an oscillatory charge. The current now tends to reverse but in so doing extinguishes the thyratron; the cycle of events is shown in figure 1 (*d*). Thus the voltage V_{ab} across *T* and *C* has a suitable form for the modulating bias, with peak values up to 2000 volts, and the pulse length can readily be altered by varying the product *LC*. The value of *L C* must be so chosen as to keep the peak current through the thyratron below the limit, in this case 0·6 A., and the operation is considerably steadier if it is kept well below this figure. The voltage across the choke collapses very rapidly, in fact it oscillates with the natural frequency of the choke as shown with small dots in figure 1 (*d*),

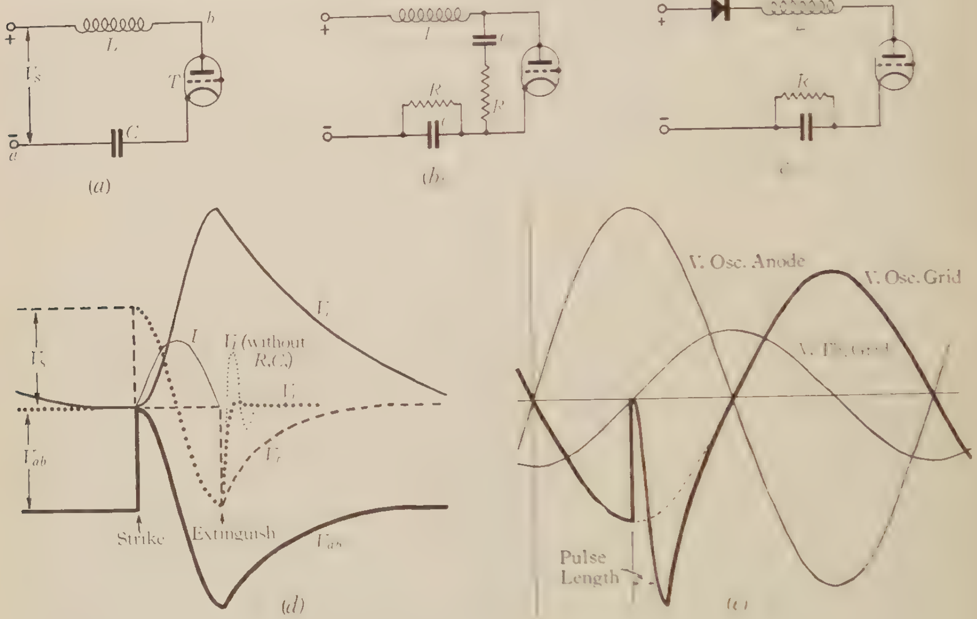


Figure 1.

so that the bias may fall nearly to zero and cause the oscillations to build up again. The simplest way out of the difficulty is to connect a condenser C_1 in series with a resistance R_1 across the thyratron as in figure 1 (*b*). This will have no effect while the thyratron is conducting, except to increase the peak current through it, but when it extinguishes, *C* discharges through the condenser C_1 and resistance and the choke, so that the voltage across the latter, shown by large dots in figure 1 (*d*), is no longer oscillatory. This arrangement is simple but it is not positive, and in the event of its failure the transmitter either oscillates continuously or squeggs, having to charge up the condenser across the supply circuit. When the oscillating valves are used at the voltage limit as in this case the possibility of failure cannot be entertained, for the dissipation limit is not far away even with the short pulses employed. If a rectifier is inserted in the supply lead before the choke, as in figure 1 (*c*), then any grid current or any charge on the grid must be diverted into the condenser C, and if the oscillations are not fully quenched this condenser becomes the reservoir condenser of a squegging circuit and the oscillations must be quenched by the squegging. If this rectifier is of the gas-discharge type it will not appreciably affect the oscillatory nature of the charge of C, and the pulse length is controlled entirely by the modulating circuit. If a thermionic rectifier is used the arrangement gives a compromise between the above conditions and a positively-controlled squegging oscillator.

To ensure that the condenser C is completely discharged just before the beginning of the pulse it is necessary to connect a leak R, figures 1 (*b*) and 1 (*c*), across it, and the limits of the time constant of this combination depend on the nature of the supply to the anodes of the oscillating valves. If the supply is a.-c., then the holding bias also can conveniently be alternating voltage of suitable magnitude and 180° out of phase with it. The thyratron is tripped when the anode voltage is at its maximum positive value, again by an alternating voltage which leads the thyratron anode-voltage by 90°. The time constant RC must then be not less than one-quarter of a cycle, corresponding to a time of 5 msec. for a frequency of 50 c./sec.; it must also be well below 10 msec., otherwise the condenser will not be fully discharged by the time the next pulse is due to occur. The range of values is quite limited and care must be taken to ensure that it shall not vary beyond this range with variation of the humidity, etc. Figure 1 (*e*) shows the cycle of events in a system operated entirely by the a.-c. mains supply.

With d.-c. supply to the anodes of the oscillating valves, the holding bias must be maintained except for the short time during which the pulse is being generated, and the voltage across the thyratron must be maintained over the same period, for, though it is negative at the moment of quenching of the oscillations, it returns fairly rapidly to positive values. The tripping pulse for the thyratron must be quite short, of the order of 1 msec., and this figure is then the lower limit for the required time constant. The range of values in this case is much less restricted.

A convenient circuit for obtaining the tripping pulse for the thyratron is shown in figure 2. An a.-c. voltage of about 100 is applied through the primary of a transformer to the anode of a valve of the small-output type used in receivers, and to the grid of this valve is applied an a.-c. bias, leading the anode voltage by nearly 90°, from the network L, R, C, as shown. When the grid becomes negative, the sudden stoppage of anode current causes the voltage across the transformer to rise, and the voltage across the secondary, together with the necessary steady bias, is applied to the thyratron grid. This scheme gives a pulse of duration 0·5 msec., in shape approximately half of a sine wave, and seems preferable to the usual devices for deforming wave-form, with which the point of tripping is likely to be erratic. The primary inductance and self-inductance of the transformer should be kept low and the external circuit of the secondary should be purely resistive, or the pulse will be unduly lengthened. A resistance is connected in series with the grid of the thyratron to limit the current when the arc strikes.

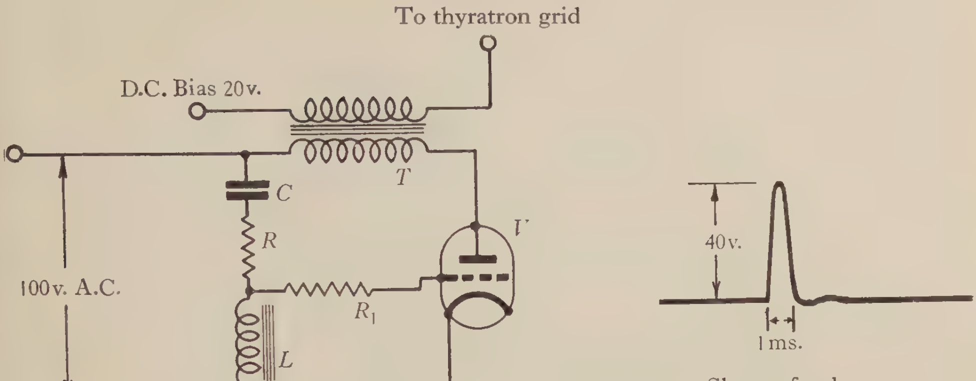
A suitable modulating bias having been obtained, it has to be applied in the most efficient manner to the grids of the oscillating valves. In the complete schematic diagram of the transmitter, figure 3, it is seen that the steady bias reaches the grids through the resistances R_3. If a short pulse is applied to the grids through these, it will be considerably distorted and the voltage on the grid will fall relatively slowly. Now the time taken for the oscillations to build up to a given value depends on the initial disturbance, or on that part of the disturbance which occurs in the first half-cycle of the oscillation. It is therefore necessary to apply the steep initial portion of the modulating pulse to the grids in the shortest possible time. This involves the provision of a capacitive path as well as the resistive one; a condenser across R_3 would short-circuit the radio frequency drive on the grids, but the connexion of the centre point of the tuning-condensers C_1 to the centre point of the resistances R_3 provides the required capacitive path, if the bias is applied between this point and the filaments. The impulsive kick on the grids can be regarded as a sharing of charge between the grid-filament capacities and the other capacities in series, and, with the values in use, it is found that only about three-quarters of the full amplitude of the impulse gets on to the grid immediately, and that this may still not be enough to bring the bias to the point where the oscillations build up at the maximum rate, i.e. to the straight portion of the grid-volts, anode-current characteristic of the valve. It is necessary then to bring the connexion from the filaments to a potentiometer connected across the terminals which supply the modulator circuit, and to provide a capacitive path across one side of this, which accounts for R_8, R_9 and C_9.

§ 5. THE RECEIVING SYSTEM

The pulses are received on an inverted-L aerial with a long horizontal portion and only enough down-lead to give the requisite strength to the reception of the ground-ray. This aerial is coupled to a receiver of the type designed by Dr G. Builder for this type of work(4). The output from the linear detector is fed direct to one pair of plates of the cathode-ray oscillograph, with the time-base on the other pair, and the lay-out is arranged for visual observation and for photographic recording.

§ 6. THE SYNCHRONIZATION PROBLEM

Preliminary considerations of the possibilities and requirements of a locking arrangement for use in this work have already been indicated. The first scheme which occurs to mind is to have extremely stable oscillators controlling the recurrence-frequencies of pulse and time-base. In this case we can be sure that the difference in frequency between the two oscillators will never be large and we can make the locking effect very slight, so that random disturbances will not affect the frequency or phase of the controlled oscillator to any great extent. If the locking effect is small, however, considerable phase-variation between the two oscillators is possible for small variations in the natural frequencies, and this will cause the trace of the ground-ray to wander in position along the time base; but



Shape of pulse

Figure 2. Circuit producing short d.-c. pulses.

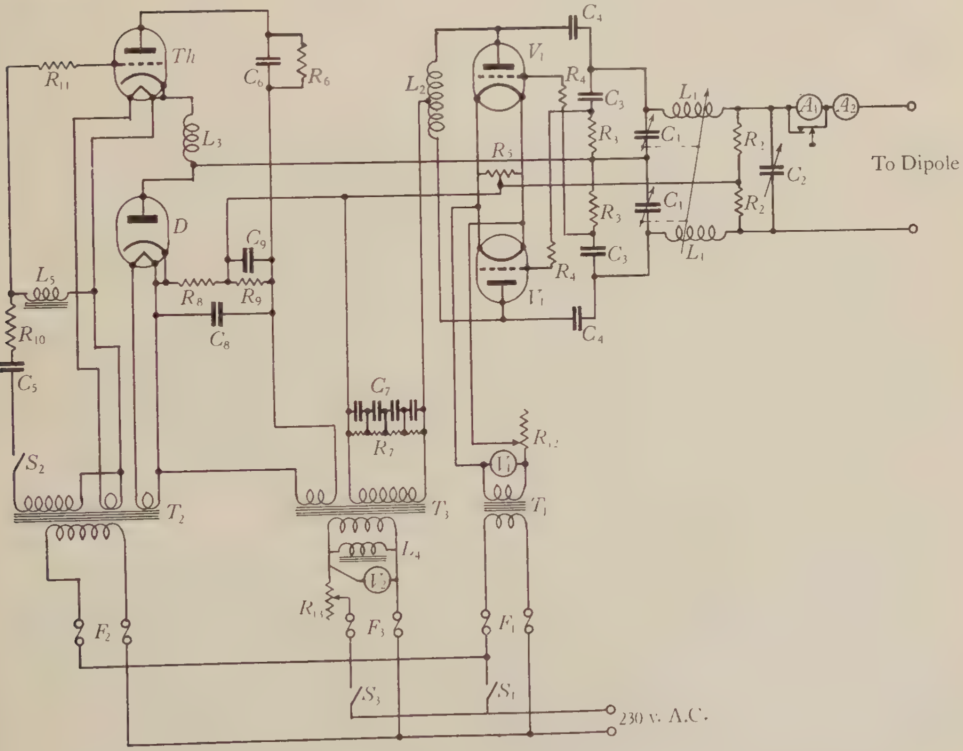


Figure 3. Radio-frequency pulse-transmitter.

the necessary compromise still retains the feature of insensitivity to random disturbances. The use of two such oscillators would be expensive and will be shown, after comparison with other schemes, to have negligible advantage for the purposes in view.

Another case arises when the recurrence-frequency of the pulse is, of necessity, rather variable, for instance when it is controlled from the a.-c. mains. At the receiver we must have a control oscillator which can be made to follow these variations. It is impracticable to adjust the natural frequency of the time-base control oscillator by means of the received pulse, but it is possible to adjust its phase, or to speed it up during a portion of its cycle. We should prefer to start the time base just a little before the arrival of the ground signal, so that we could observe and measure from the beginning of the pulse. But since the pulse itself has to provide, even if indirectly, the necessary speeding up or phase-adjustment of the control oscillator, the phase of the point in the local cycle of events just before the arrival of the pulse, relative to the phase of occurrence of the pulse in the cycle of events at the transmitter, will vary as the frequency varies. Thus a continuous record of the layer-height is likely to show considerable variations of the base line (the ground-ray trace) and this would make the interpretations of heights more difficult and the variations thereof much less obvious.

The only way out of this difficulty is to make the arrival of the pulse the beginning of the cycle of events at the receiver, in other words to make the pulse start the time base on its sweep. This entails the loss of a portion of the beginning of the pulse and we are left with some uncertainty in the measurement of heights. But since the apparatus will lock satisfactorily with a pulse-amplitude only one-tenth of that normally used, and since the duration of the upstroke is only about 0·1 msec., the error in time is not greater than 0·01 msec. plus the time taken for the time base to start on its sweep, which is not more than 0·01 msec. Now 0·02 msec. corresponds to a height of 3 km., which is of the order of accuracy in measurement under any circumstances. With this arrangement the pulse always occurs at the beginning of the time base and so gives a straight line on continuous records. If the above error cannot be tolerated, then we are forced to use the previous scheme and to put up with the uncertain position of the ground pulse; this uncertainty in turn introduces its own errors, unless the time scale is very uniform or the calibrating marks are very close.

The next point for consideration is the interference due to random disturbances, to which is closely allied the tendency to lock on echoes rather than on the ground pulse. This latter effect is discussed elsewhere(5), and a circuit is given for overcoming the difficulty; but it can be overcome more simply by the use of a thyratron, as will be shown later. The following discussion is not concerned with the actual procedure adopted. The first echo to be received may, on occasion, be as much as 4 msec. later than the ground pulse; it may be extremely wide, and never fade completely to zero. If by chance this late echo should be in a position to cause locking, the ground ray must be capable of regaining control, or long periods of the record will be valueless. If we cater for this eventuality, then, when the time base is correctly locked on the ground pulse, any disturbance occurring 4 msec. before is capable of taking control. If the ground pulse is not above the general noise level the position is hopeless, for discrimination between random disturbances and the recurrent pulse over a period of 4 msec. is impossible.

Normally there are echoes of much less delay and, though an individual echo may be as much as 10 msec. later than the ground ray, echoes before it will successively take control until the ground pulse is able to do so. If an observer is present he can take care, by manual control, of the relatively rare contingency discussed above, but for purely automatic recording of the critical conditions of the Appleton region it is preferable to design on the basis of this figure of 4 msec. for the delay of the first echo. Even in a scheme using extremely stable oscillators for control purposes at transmitter and receiver, opportunity to lock on an echo is sure to be given when atmospherics are bad, and if the scheme is designed on the basis of the above figure, it loses its main advantage, i.e., its discrimination against random disturbances.

The displacement of the pattern due to a disturbance prompts an investigation of the time efficiency of the system, i.e., the proportion of the total time during which the pattern is in its correct position. A scheme giving the greatest time efficiency over short periods does not necessarily give the best efficiency over long periods, but it gives at least as much information so that short-time efficiency must be the criterion. In the type of P', f records taken in this laboratory a period as short as 15 sec. is allowed at each frequency and at least 5 sec. of this must be allotted to changing of frequency and retuning. If therefore the pattern should be displaced, it must take up its correct position in much less than 10 sec., preferably in less than 1 sec.; the lower limit is 0·1 sec., set by the 4 msec. over which the pulse must be effective in locking. In actual practice, the figure can be made as low as 0·2 sec., and no manual control could bring it into position as quickly as this. Even for a value of 0·5 sec., the difference in natural frequencies of the two control oscillators becomes 2 c./sec., when frequency-variations as great as 1 per cent become negligible. This consideration nullifies the advantages of the stable oscillator scheme.

§ 7. THE SYNCHRONIZING SYSTEM

With the general considerations outlined above in mind, the arrangement shown in figure 4 was devised. A tuned circuit L, C is maintained in oscillation by the valve V_1 at a frequency of about 50 c./sec.; a certain amount of drive is also derived from the anode circuit of the thyratron V_3, as is apparent from the diagram. The amount of this drive is controlled from the pulse itself, the oscillator being thus synchronized with the recurrence frequency of the pulse. A portion of the oscillatory e.m.f. is applied to the grid of the valve V_2, which then acts as a switch for the thyratron. It has been found quite feasible to effect the extinction of the thyratron arc by grid voltages of the order of one-quarter of the anode voltage, for currents through the thyratron up to 50 mA., provided that the voltage on the anode cannot rise when extinction occurs. The thyratron thus regains some of the advantage of the thermionic valve, in that both the conducting and the non-conducting states can be controlled by the grid.

By a suitable choice of the resistance-capacity circuit R_2, C_2, R_{12}, in the anode circuit of V_2, a voltage cycle of square form is obtained across R_2 when a sine wave is impressed on the grid, and this is capable of tripping and extinguishing the thyratron at the appropriate instants. The inductive load L in the thyratron anode circuit would give a rise in voltage at extinction, but this rise is limited by the resistance-capacity circuit R_3, C_3, across the thyratron (whose primary function, however, is to switch the time base) and also any rise of voltage across the inductance would cause the other valve V_1 of the push-pull circuit to become conducting, so that it is doubly safe-guarded. The negative pulse from the receiver is also impressed on the grid of V_2 through the terminal P, and if it occurs before the grid has acquired a negative charge under the influence of the control sine wave from the oscillator, it causes the thyratron to strike sooner than usual and the oscillator is speeded up. Should the pulse occur too soon, so that the grid of V_2 goes positive again under the influence of the control voltage, the thyratron is duly extinguished but the locking effect is so considerable that the oscillator is speeded up till the pulse is in the correct position. A disturbance occurring at such an early stage merely registers as a gratuitous ground pulse, but does not affect the time scale because the condenser of the time-base circuit discharges almost immediately on the extinction of the thyratron and conditions are always the same (the condenser is always discharged) at the beginning of the time base proper. The

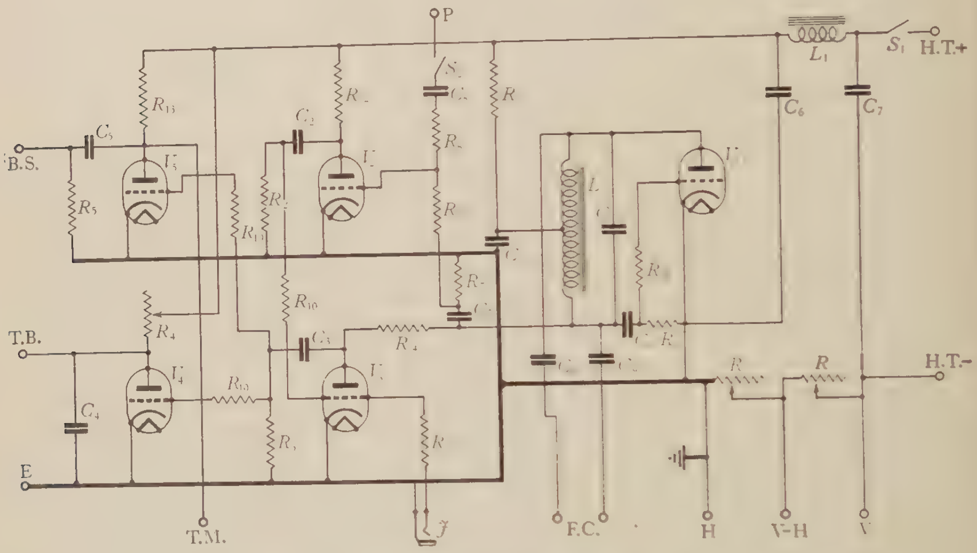


Figure 4. Pulse-synchronized time-base circuit.

direct induction into the receiver from the thyratron is not serious, except occasionally when the latter is near the end of its life.

The resistance-capacity circuit R_3, C_3 across the anode circuit of the thyratron gives a voltage cycle across R_3 of much squarer wave-form than that across R_1, and this voltage controls the time base. The time base valve V_4, then, is conducting, and the condenser C_4 is discharged, till the thyratron strikes; when the pulse arrives and trips the thyratron, all anode current through the valve V_4 is cut off and C_4 charges through the resistance R_4. The voltage across C_4 is taken to one pair of plates of the oscillograph and constitutes the time base. Thus the pulse always occurs at the beginning of the time base and it has been shown that the portion not registered is of the same order as the accuracy of measurement. It should be noted that the amplitude of the pulse necessary to trip the thyratron depends on the amplitude of the control voltage on the grid of V_2, and on the difference between the natural frequencies of the control oscillators at the transmitter and the receiver or the tightness of locking. The portion of the pulse lost as a result of the use of this system depends on the above two factors and also on the steepness of rise of the pulse. The estimated value of 10 μsec. for the time lost in actual operating-conditions is readily attainable.

The valve V_5 is controlled in like manner to V_4 from the resistance R_3, but the resistance-capacity connexion R_5, C_5, R_{13} in the anode circuit is so chosen as to give a square wave-form across R_5. This voltage is applied to one of the other pairs of plates of the oscillograph, so that the backstroke of the time base is deflected in the opposite direction to the pulse and is therefore removed from the field of the camera. Two pairs of coils on a suitable core of transformer-steel stampings are connected in the high tension negative lead to the unit, with a variable resistance R across each pair, to provide a ready means of adjusting the time base both vertically and horizontally. This arrangement eliminates origin-distortion in the oscillograph.

An exponential time base has been used for the sake of simplicity and because it gives a greater range of heights for a given accuracy of the lowest height. It can be taken as uniform over 100 km. and, since marks for every 50 km. appear on every photograph, non-linearity is no drawback.

The frequency of the local control oscillator, and thus indirectly the amount of locking, is controlled by a variable resistance (connected externally to the terminals F.C., and placed in the manner convenient for the operator) in series with the condensers C_9, connected across the oscillatory circuit. This method of control introduces a variable load into the oscillating circuit but is more convenient than a variable condenser, which would have to be inconveniently large.

If at any time it should be requisite to have the whole of the pulse on the time base, e.g. when maximum accuracy in height-measurement is essential, it is only necessary to control V_4 and V_5 from the oscillatory circuit, so that the voltage is slightly dephased, in order to start the time base before the arrival of the pulse. The locking process functions as before and there is no distortion of the time scale, but any variation of the recurrence-frequency of the pulse will cause the ground-ray to wander in position, as has been pointed out above. The amount of locking and the degree of discrimination between pulse and disturbance are fixed by a suitable choice of R_{14}, R_{10} and R_8.

Since no steady bias is used, from considerations of simplicity and economy, the phase of striking of the thyratron is considerably later than that of zero e.m.f. in the oscillatory circuit, although this point would give the optimum locking effect. The voltage on the grid of V_2 is advanced in phase by the resistance-capacity combination R_7, C_7 to compensate for this defect.

Resistances of the order of 250,000 Ω. are inserted in series with all grids to limit the flow of grid current when such high positive biases are used. A short-grid-base valve such as the MH_1 type is used for the control valve, since it gives a sharper wave-form in the anode circuit for a given grid voltage, and the small power type (AC/P) is used for V_4 and V_5, where the d.-c. resistance is the important factor.

The unit is run entirely from the a.-c. mains supply and, since the local control frequency is only slightly different from the local supply frequency, the smoothing in the eliminator circuit must be considerably more efficient than is usual. In this connexion it may also be mentioned that the commercial type of high-tension supply units for cathode-ray oscillographs require additional smoothing.

§ 8. CALIBRATION OF THE TIME BASE

A calibration of the time base is necessary, and the usual procedure is to photograph at intervals the output from an oscillator, which is deformed if preferred and is applied to the oscillograph in place of the echo pattern. With an exponential time base it is preferable to make the reference points as numerous as possible, so that a frequency of 3000 c. sec. is suitable, for then each complete cycle represents 100 km. of path or 50 km. of height. This calibrating oscillator is usually locked to a harmonic of the time-base recurrence-frequency, but, as was mentioned above when the locking of the control oscillator to the pulse recurrence-frequency was being considered, there must be some phase-variation between the two oscilators, so that the markings bear no fixed relation to the beginning of the pulse, and this point is not available for measurement in the scheme outlined above. The difficulty is eliminated if one of the time marks is made coincident with the arrival of the pulse or the beginning of the time base; this requires that the condition in the calibrating oscillator shall always be the same at the beginning of each time-base sweep, and the simplest and most reliable condition is that of quiescence. Then the oscillations should be started by some event coincident with the beginning of the time base, attain a reasonable amplitude in as short a time as possible, and maintain it for the duration of the time base.

The voltage on the grid of the thyratron is of a suitable form for controlling such an oscillator in that it is very negative before the commencement of the time-base sweep and practically zero during it. The grid of the oscillating valve V_1, figure 5, is therefore connected (by a jack lead) to that of the thyratron through a resistance R_{15}, figure 4, of about 250,000 Ω., and another similar resistance R_1, figure 5, is connected from the grid of V_1 to its oscillatory circuit. This arrangement is found to be very satisfactory, the oscillator attaining its maximum amplitude in about 5 cycles and decaying completely in about 5 msec.

Since this time-marking will always be fixed in position relative to the beginning of the ground pulse, it can advantageously be superimposed permanently, provided that the echo pattern is not unduly distorted in consequence. Two stages of wave-form deformation are required, as shown in figure 5; the full oscillatory voltage is applied to the grid of V_2 through the limiting resistance R_6, and a very peaked wave-form is obtained across R_3 by suitably adjusting the values of R_5, C_3 and R_3, in the anode circuit. The voltage across R_3 is applied to the grid of V_3, and the biasing circuit R_4, C_4, in the cathode lead, ensures that current shall pass for a very short period only. The anode of this valve is connected in parallel with that of the valve V_5 in figure 4, through the terminal T.M., so that the oscillograph spot is deflected momentarily to the backstroke position and the time base appears as a discontinuous line.

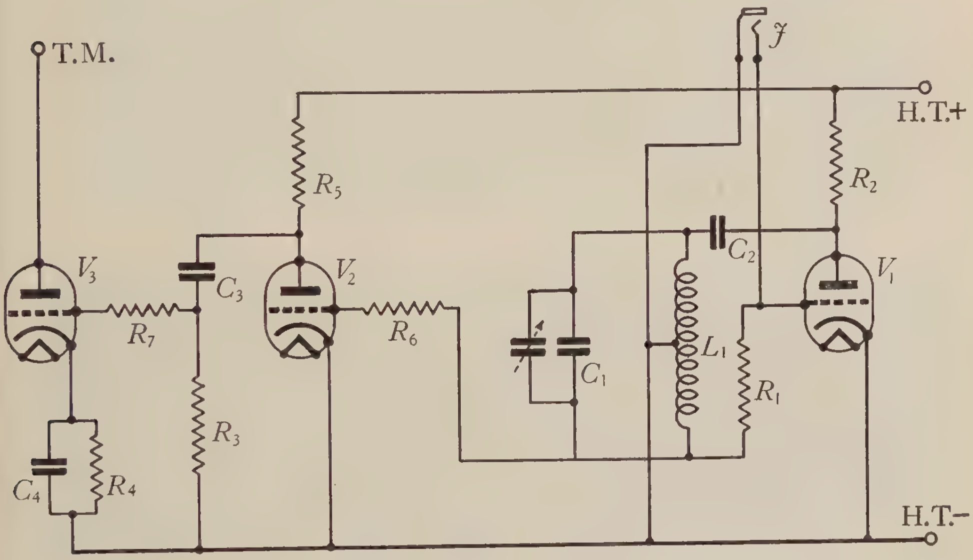


Figure 5. Calibrating oscillator.

Careful check observations, made by applying the output from a separate stable oscillator to the oscillograph in place of the echo pattern, and also by comparison of the heights of second and third order reflections, show that the equivalent height at any point as indicated by this method is in error by not more than 2 km. for heights from 100 to 1000 km., i.e., the accuracy attainable is of the order of the accuracy of measurement, when the readings are adjusted to be correct at the limits given. The 50-km. mark is unreliable because of the smallness of the amplitude of the oscillation at this point, but this is of no moment since echoes rarely appear below an equivalent height of 100 km.

The advantages of the scheme are numerous. Heights can be read off at once and the variations of height are immediately obvious, even if the time base alters its position in the camera field. The time scale can be varied without any necessity for a separate calibration, and any variations are automatically checked. A portion only of the time base need be kept under observation if required, without loss of accuracy. Finally, since the oscillator is not locked to a harmonic of the time-base frequency, variations of the latter can cause no error. But illustrations of the operation will give the best idea of its suitability for this type of work under the conditions imposed.

§ 9. RESULTS

In figure 6 are shown two records of the kind taken daily at the Halley Stewart Laboratory, showing the variation of the equivalent height with frequency. The frequency at the transmitter is changed by approximately 0·3 Mc. sec. every 20 or 30 sec.; at present this is still done manually, from 2 to 3 sec. being required for the change. At the receiver, the echo pattern is screened off except for a strip 1 mm. wide along the base line, so that the echoes appear as a missing part of the time base, and, when photographed, the trace appears white on a black background(6). During the retuning period the echo pattern is absent, and so a continuous black line across the record, which serves to distinguish one frequency from the next, appears. The frequency steps have been calibrated so that the frequency of each section is known, the sections being identified by means of a suitable scale. The photographic paper is moved through the camera at a speed of 2 ft. per minute by means of a small gramophone motor of the induction type, the speed of which is reasonably constant. The time required at the receiver for retuning is about 2 sec. so that a period of 15 sec. is available for recording at each frequency, and this is long enough to ensure a fair sampling of conditions. These figures permit us to cover the range 2·4 to 6·0 Mc. sec. in half an hour; the time spent on each frequency can be reduced to 15 sec., but this leaves no margin for accidents, and it is unwise to lengthen the time, for temporal variations in height may be considerable.

The amount of detail available in these records is at once obvious, and it is usually possible to identify the critical frequencies of both the ordinary and the extraordinary rays for all the reflecting regions, of which as many as five components appear on some records.

In the upper record in figure 6 the ordinary ray first appears in the lower E region (E^{I}) at a height of 120 km., rising suddenly to the intermediate region (E^{II}) at 140 km., later passing to the F region at 210 km. and finally penetrating this also. The nomenclature adopted for the various regions is that suggested by E. V. Appleton(7). The extraordinary ray follows the same procedure, but always makes the jump at a higher frequency, the actual value of the separation being about 0·7 Mc./sec. for each of the three regions, indicating that electrons are predominant over ions in all regions. The vast majority of records show this normal separation for all regions, but the lower record of figure 6 shows a definite departure from the value of 0·7 Mc./sec. For the ordinary ray, there is a trace of reflection from an intermediate region and then the obvious jump to the *F* region which it penetrates in the usual way. The extraordinary ray, however, appears to penetrate the *E* region about 1·4 Mc./sec. later than the ordinary ray, though it penetrates the *F* region with the normal separation. A multiplicity of echoes is to be noted just after the ordinary ray has penetrated the lower layer; it is possible to distinguish the first, second and third reflections coming from region *E*, and the first and second coming from *F*, together with another echo which must be interpreted as the *M* reflection postulated by Ratcliffe and White⁽⁸⁾, i.e., a ray reflected twice from the *F* region and once from the upper surface of the *E* layer. This type of reflection is commonly associated with the delayed critical frequency of the *E* region as illustrated in this record.

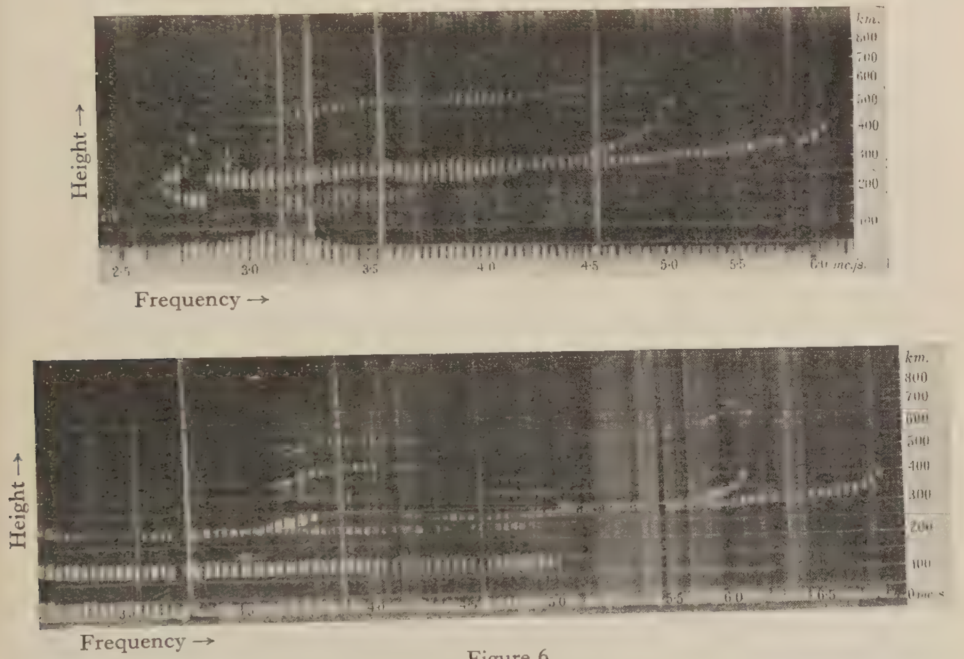


Figure 6.

In the lower record of figure 7 is an example of a *P*′, *t* trace, wherein the frequency of the transmitter is fixed and the paper in the camera is moved continuously, so that the variation of the equivalent height with time is recorded. The height-calibrations are very well reproduced in this record, the distance between each of the fine horizontal white lines being equivalent to 100 km. in path or 50 km. in height. The extraordinary ray is to be seen at a height of 300 km. and the ordinary ray varying from 350 km. upwards; this component itself splits into separate components, and on occasion these can be observed to cross and recross each other, as indeed they appear to do in this record. The beginning of the ground pulse does not reproduce very well on the photographs, but in the originals it can be distinguished as a fine black line at the lower edge of the record.

The upper photograph is a record taken when no ground-ray was present; it will be seen that we can get the equivalent heights from the distance between the first and second reflections, and from these data the height of the other component can be deduced. Though these records have been taken under conditions which are probably better than normal, it is possible to follow in the originals the traces of echoes even when the disturbances are so bad that the signal is not distinguishable by ear from the general noise.

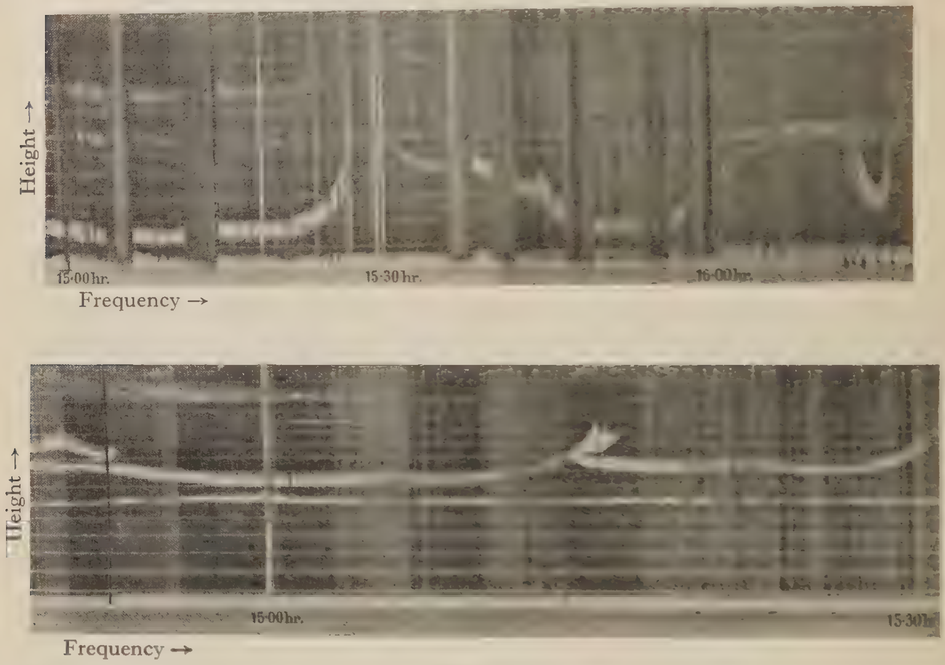


Figure 7.

§ 10. CONCLUSION

It has been demonstrated that, even when there is no common control frequency available at both transmitter and receiver, it is quite feasible to obtain records containing almost as much information as under the very best conditions, the sole proviso being that the ground signal must always be somewhat above the general noise-level. A very definite advantage is conferred in those cases where the disturbances are due to such causes as domestic appliances run from the local mains supply, when they may occupy almost the whole of the cycle, for no amount of phase-shifting can then keep them off the echo pattern.

§ 10. ACKNOWLEDGMENTS

The work described in this paper was carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research. I wish to express my indebtedness to Prof. E. V. Appleton for initiating and providing for the construction of the apparatus, and for his continued help given by way of suggestion and criticism; to Dr G. Builder who evoked many helpful discussions while engaged on similar problems; to Dr E. G. Bowen, for a number of suggestions; and finally to Messrs Lordon and Roberts, for help in operating the transmitter and receiver respectively.

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THE MAGNETIC SUSCEPTIBILITIES OF THE ANHYDROUS AND HYDRATED SULPHATES AND DOUBLE SULPHATES OF THE MAGNETIC METALS: WITH A NOTE ON THE INCREASED SUSCEPTIBILITY PRODUCED BY HEATING COBALT SALTS

By E. F. HERROUN, F.I.C.

Received April 22, 1934.

ABSTRACT. It has been recognized for many years that the molecular susceptibility of many salts, particularly sulphates, is greater in the hydrated than in the anhydrous condition. Measurements of susceptibility for anhydrous and hydrated single and double salts have shown that the increase is not a specific property of water but that when potassium or ammonium sulphate is substituted for the "water of constitution" there is an increase in molecular susceptibility. With the sulphates of iron, cobalt and nickel this increase is greater than that due to a molecule of water. With manganese sulphate the difference is small but in the same direction, but with copper sulphate a molecule of water increases the susceptibility to a greater extent than a molecule of potassium or ammonium sulphate.

Note relating to the increase in susceptibility of cobalt salts after being strongly heated. The effects observed by A. Serres and by A. Chatillon have been examined and an increase in susceptibility after heating has been found, but in certain salts this is complicated by the fact that hydrolysis or oxidation occurs with the production of basic salts or oxychlorides which also cause an increase in susceptibility. Cobalt pyrophosphate appears to be stable when heated in air to 600° C. and exhibits an increase in susceptibility free from complications.

§ 1. INTRODUCTION

When Wiedemann about 70 years ago put forward his additive law, he quite clearly recognized that chemical changes may entirely alter the magnetic properties of substances. He was the first to mention* that a magnetic compound could be produced from two diamagnetic elements, copper and bromine. He also specially drew attention to the fact that the atomic magnetism of hydrated oxides and salts is, in general, greater than that of the corresponding anhydrous substances.

He stated that the magnetic properties of cobalt and nickel cyanides disappear when these bodies are dissolved in potassium cyanide, and concluded that this would not have happened if they had merely formed double salts.

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* *Comptes Rendus*, 67, 833 (1868) from *Monatsberichte d. König. Preuss. Akad.* July 1868.

Mlle E. Feytis* appears to have been the first investigator to measure in modern units the susceptibilities of hydrated and anhydrous copper sulphate and came to the conclusion that the molecule of water of constitution increased the susceptibility, while the four additional molecules in $CuSO_4.5H_2O$ were merely additive and behaved diamagnetically. F. W. Gray and W. M. Birse† came to a similar conclusion in regard to copper sulphate, saying that the first molecule of water increased susceptibility by 11·5 per cent, while the further addition had no marked effect.

As Graham had shown about a century ago that in salts of that kind the water of constitution could be replaced by the neutral sulphate of an alkali metal, it appeared of interest to determine whether, for example, when potassium sulphate is left in combination with a sulphate of one of the magnetic metals the susceptibility is that of the anhydrous salt or whether it is increased in a manner analogous to the effect of water of constitution.

§ 2. APPARATUS

Two modified forms of the Curie balance have been employed; the first and older balance had a thin phosphor-bronze suspension 15 cm. in length, and the observation was made by directly reading the number of degrees turned through by the torsion head in order to pull the specimen out of the gap between the poles of the fixed magnet. It was furnished with two permanent magnets of different strengths and an electro-magnet, any of which might be used, and in this way it covered a very wide range of susceptibility when the field was varied. But the rotation was difficult to read much more closely than to half a degree, so that with small deflections the accuracy was not very great.

Instead of this direct-reading instrument a reflecting one has been employed somewhat like the Curie-Cheneveau‡ balance but with a differently shaped magnet which is caused to slide along brass rails by means of a long brass screw having 20 threads to the inch. The arrangement used by Cheneveau, in which the magnet is moved in an arc concentric with the suspension of the radial arm, has not been followed. I freely admit that this arrangement has the great advantage of keeping the specimen in the centre of the gap even when large deflections are used, but the method of rotating the magnet by means of an arm or yoke with tiller lines or reins as described by Cheneveau did not seem to possess the requisite mechanical exactitude or delicacy. The application of gearing that would be free from back-lash and at the same time not excessively slow presents a difficulty, but not an insuperable one. This principle seems to possess great advantages and if the present instrument were reconstructed a circular motion would be adopted.

The drawback due to the relative shift of the specimen along the y-axis with the rectilinear motion of the magnet along the x-axis is partly met in the present instrument by the wide pole-gap (16 mm.) relative to the diameter of the specimen tubes (8 mm.) and by the small angular displacement of the balance arm, which is not more than 6° on either side of the zero position and frequently much less.

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* *Comptes Rendus*, **153**, 668–71 (1911).

† *J. Chem. Soc.* **105**, 2707 (1914).

‡ *Proc. Phys. Soc.* **22**, 343–59 (1910).

In the instrument described by E. Wilson* the straight-screw method was used, but in that case an electromagnet was employed: where a battery of large accumulators is available and the current can be regulated by large resistance frames, such as are met with in an electrical engineering laboratory, the variation in the resistance of the copper coil of the magnet due to heating may become negligible; but even then the current has to be very accurately read, for its value must be squared since the pull varies as H^2. Also the change in the reluctance of the iron core and pole-pieces for different excitations must be taken into account by plotting a calibration curve for H. Thus the constancy of a permanent magnet as used in the Curie-Cheneveau balance has much to recommend it.

The magnet used in the present instrument was last magnetized 12 years ago, so it may be considered to have reached a steady state. Its poles are 5 cm. deep, slightly coned, and the flat opposed faces are 12·5 mm. wide and 16 mm. apart. The strength of field in the centre of the pole-gap was measured and found to be 530 c.g.s. units; actually in the position in which the pull on the specimen is a maximum, the value of H is somewhat less than 500, but for comparative purposes the field-strength may be taken to be about 500 units.

Thin-walled soda-glass tubing of external diameter 8 mm. was used for containing the specimens throughout all these measurements. The glass was found to be diamagnetic, with a very small negative susceptibility of approximately $-0{\cdot}06 \quad 10^{-6}$, a value so small that when the strong suspension was used no deflection could be read and with the weak suspension the double deflection was only 3 mm. on a scale at a distance of 1 metre. These suspensions were of phosphor-bronze strip 0·85 mm. wide and the weaker one gave 6·8 times the sensitivity of the strong one.

So long as the quantity of substance occupied from 2 to 4 cm. of the length of the tube the force was found to be proportional to the mass, but any length greater than 4 cm. showed a slight diminution due to the fringing of the magnetic field near the top and bottom of the magnet poles. It will be seen that with a substance occupying 4 cm. there was 0·5 cm. between the top and bottom of the specimen and the limits of the magnet poles, 5 cm. deep.

§ 3. SOURCES OF ERROR

The most common source of error in the use of magnetic balances of this type appears to lie in the use of specimens or containers of different diameter: as $H_y . dH_y/dx$ has a maximum over a very narrow belt on each side of the magnet poles, any appreciable increase in diameter must necessarily cause some part of the section of the specimen to lie in a part of the field which is farther from the zone of maximum force, with the result that lower readings for susceptibility with larger diameters are inevitable. Any substance with a susceptibility so great that it materially alters the distribution of the lines in the field is obviously unsuitable for measurement with this form of instrument. The scale, which was divided into millimetres, was bent into a curve of radius 1 m. and situated 1 m. away from the mirror attached to the bar carrying the specimen. The mirror was concave of focal length 1 m., and a collimating lens was used in front of the narrow slit. The position of the edge of the image could easily be read to 0·5 mm., or even more closely, but the deflections on repetition were rarely more constant than to 1 mm. though they could be relied upon to that extent.

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* *Proc. R. S.* A, **96**, 429–55 (1918).

On a deflection of 300 mm., the error would not be greater than 1 in 300. The results for the mass susceptibility are therefore usually given to only 3 significant figures, but when a mean of several readings has been taken a second place of decimals is sometimes given though without any claim to great accuracy. When the weak suspension is used the results are shifted nearly 10-fold but the fourth figure, when given, is still doubtful.

The arm carrying the specimen was of aluminium and counterpoise weights were arranged so that they could slide along the arm on the side opposite the specimen. This arm was fully 2 cm. above the magnets when the strong suspension was used and 3 cm. when the weak one was used: no deflection due to the arm alone was observed.

There was however a small possible error worth recording, due to the fact that when not in use the magnet had a soft-iron armature placed across its poles; when this had been in position for a day or more, on its removal the instrument gave with a standard specimen a slightly greater deflection than normal, but after about half an hour the deflection was found to have recovered its usual value after which it remained constant for many hours. Even an aged magnet may have its magnetic flux temporarily increased by the use of an armature.

§ 4. SPECIMENS AND RESULTS

The salts used were of a high degree of purity, generally recrystallised, and nearly all the double salts were specially prepared for this research. The water of hydration was checked by weighing before and after dehydration. The latter process, in certain cases, was carried out in a current of dried carbon dioxide to prevent oxidation and in certain cases in a vacuum to prevent access of oxygen and also to remove the water vapour as quickly as possible. Details are given later.

All the salts of manganese, iron and cobalt and many of those of nickel and chromium were measured with the strong suspension, but some of the latter and all the copper salts were measured with the weak suspension to obtain the necessary sensitivity.

The susceptibility employed as a standard does not depend on the selection of some particular salt, but partly upon the absolute constant for the instrument found by my old friend and colleague the late Prof. Ernest Wilson in the paper already referred to. It also depends upon tests carried out with this and another instrument* devised by him. Various specimens were measured by both of us, in my case with a reflecting magnetometer and also with the balance first mentioned in this paper. In this way an average constant and standard of susceptibility were arrived at.

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* *Proc. R. S.* A, **98**, 274–84 (1920).

As one of the chief objects of the present inquiry was to examine the paramagnetic effect, if any, of intrinsically diamagnetic salts as compared with water, no allowance has been made for the negative susceptibility of any of the constituents, and the results are calculated for columns 4 and 5 of the table as if only the active constituent had any magnetic effect. By "active constituent" is meant the molecular proportion in a given salt of the sulphate of the magnetic metal concerned.

χ_M The product of the molecular weight and mass susceptibility χ_M has been given to four significant figures, but here again no reliance can be placed on the last numeral: in the case of ferric and chromic salts, half the molecular weight has been taken to bring them into line for comparison with the divalent salts.

The results are given in table 1 and special remarks will be found under the headings of the different metals. The general conclusions are then stated and the remarks concerning the anomalous results obtained from heated cobalt salts are given in a separate note.

No magneton numbers have been tabulated since Δ, in the Curie-Weiss equation, $\chi_M (T + \Delta) = C$, is commonly unknown and is probably positive in some and negative in others of the salts examined. An approximation to the magneton number may, however, be obtained either by the equation used by S. Meyer*, or by a modification which may be more simply written and easily remembered, viz: Weiss magneton number $= 240 . \sqrt{\chi_M}$, where the latter figure is expressed in c.g.s. units as in column 5 of table 1.

§ 5. REMARKS ON TABLE 1

Iron. Ferrous sulphate heptahydrate, and ferrous potassium and ferrous ammonium sulphates were dehydrated in a current of dried carbon dioxide to avoid oxidation; in this way white anhydrous salts were obtained. It is not possible to dehydrate ferric ammonium sulphate (iron alum) as it decomposes before dehydration.

It will be seen from column 4 of table 1 that ferrous sulphate has the highest value for its susceptibility in the form of ferrous ammonium sulphate, and next to it comes ferrous potassium sulphate both hydrated and anhydrous.

Anhydrous ferric sulphate has the low value of $57{\cdot}4 \times 10^{-6}$ rising to $75{\cdot}45 \times 10^{-6}$ in the form of iron alum. Magnetic dilution has evidently a great effect in both ferrous and ferric salts, and with the former both potassium and ammonium sulphate cause a greater increase in susceptibility than several molecules of water.

Manganese. In the sulphates of this metal the value of χ_M is increased only slightly by one molecule either of water or potassium sulphate, the maximum being reached with the greatest magnetic dilution in $MnSO_4 . 5H_2O$ or in $MnSO_4 . K_2SO_4 . 4H_2O$.

As manganese sulphate can be safely dehydrated by heating in air to about 300° C. its constancy renders it useful as a standard of reference, for when sealed in a glass tube it must remain unaltered indefinitely.

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* *Phys. Z.* **26**, 51–4 (1925).

Table 1

Formula	Temperature (°C.)	χ for salt (10^{-6} units)	χ for active constituent (10^{-6} units)	χ_M (c.g.s. units)
Iron salts				
$FeSO_4$	18·2	66·4	66·4	0·01008
$FeSO_4.H_2O$	18	64·6	72·3	0·01097
$FeSO_4.7H_2O$	17	42·4	77·6	0·01178
$FeSO_4.(NH_4)_2SO_4.6H_2O$	17	32·3	83·4	0·01266
$FeSO_4.(NH_4)_2SO_4$	18	42·8	80·0	0·01215
$FeSO_4.K_2SO_4.6H_2O$	17	28·2	80·6	0·01224
$FeSO_4.K_2SO_4$	18	37·3	80·05	0·01216
$Fe_2(SO_4)_3$	21	57·4	57·4	0·01145 for $\frac{1}{2}M$
$Fe_2(SO_4)_3.6H_2O$	19·4	58·0	67·3	0·01346 ,,
$Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$	21·5	31·3	75·45	0·01509 ,,
Manganese salts				
$MnSO_4$	17·2	92·7	92·7	0·01399
$MnSO_4.H_2O$	18	83·4	93·35	0·01409
$MnSO_4.4H_2O$	19·4	66·8	98·7	0·01490
$MnSO_4.5H_2O$	17·2	62·6	99·7	0·01506
$MnSO_4.K_2SO_4.4H_2O$	17	38·0	100·0	0·01510
$MnSO_4.K_2SO_4$	18	43·6	93·9	0·01418
Cobalt salts				
$CoSO_4$ (heated in vac.)	18·5	61·6	61·6	0·009537
$CoSO_4.H_2O$	17·5	56·7	63·3	0·009812
$CoSO_4.7H_2O$	17·2	35·9	65·1	0·01009
$CoSO_4.(NH_4)_2SO_4.6H_2O$	19	26·2	66·8	0·01035
$CoSO_4.(NH_4)_2SO_4$	20	34·9	64·7	0·01002
$CoSO_4.K_2SO_4.6H_2O$	18	24·6	69·4	0·01076
$CoSO_4.K_2SO_4$	19	32·5	69·0	0·01070
ditto after 600° C.	20	34·3	72·87	0·01129
Nickel salts				
$NiSO_4$	20	26·4	26·4	0·004085
$NiSO_4.H_2O$	20·2	24·3	27·13	0·004198
$NiSO_4.6H_2O$	20·2	16·7	28·4	0·004389
$NiSO_4.7H_2O$	19	16·10	29·22	0·004520
$NiSO_4.K_2SO_4.6H_2O$	22	10·1	28·52	0·004413
$NiSO_4.K_2SO_4$	22	14·25	30·30	0·004688
$NiSO_4.(NH_4)_2SO_4.6H_2O$	28·5	11·25	28·71	0·004442
$NiSO_4.(NH_4)_2SO_4$	17	16·25	30·19	0·004661
Chromium salts				
$Cr_2(SO_4)_3.5H_2O$	18	24·5	30·2	0·005910 for $\frac{1}{2}M$
$Cr_2(SO_4)_3.8H_2O$	18	22·1	30·2	0·005927 ,,
$Cr_2(SO_4)_3.K_2SO_4.24H_2O$	18·5	12·8	32·6	0·006390 ,,
$Cr_2(SO_4)_3.K_2SO_4.6H_2O$	17	18·5	31·8	0·006241 ,,
$Cr_2(SO_4)_3.K_2SO_4$	17·5	22·1	31·95	0·006261 ,,
$Cr_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$	22	13·25	32·3	0·006335 ,,
$Cr_2(SO_4)_3.(NH_4)_2SO_4$	20	23·3	31·15	0·006110 ,,
Copper salts				
$CuSO_4$	18·5	8·79	8·79	0·001397
$CuSO_4.H_2O$	18·5	8·91	9·92	0·001577
$CuSO_4.5H_2O$	18	6·13	9·62	0·001530
$CuSO_4.K_2SO_4.6H_2O$	18	3·26	9·05	0·001439
$CuSO_4.K_2SO_4$	18·5	4·69	9·83	0·001563
$CuSO_4.(NH_4)_2SO_4.6H_2O$	18	3·61	9·06	0·001441
$CuSO_4.(NH_4)_2SO_4$	17	4·56	8·37	0·001330

Cobalt. The value given for anhydrous cobalt sulphate was obtained from the salt after dehydration at 300° C. in a vacuum: further heating in a vacuum to 400° only increased its value of χ to $62{\cdot}2 \times 10^{-6}$. The effect of heating in air to above 600° will be considered in the note on cobalt salts.

With cobalt sulphate as with iron the higher susceptibilities are exhibited by the cobalt potassium and cobalt ammonium sulphates, the effect of potassium sulphate on the anhydrous salt being distinctly greater than that due to a molecule of water of constitution, $69{\cdot}0 \times 10^{-6}$ to $63{\cdot}3 \times 10^{-6}$.

Nickel. Nickel sulphate showed a rather smaller alteration in susceptibility but, like cobalt sulphate, showed the highest values for susceptibility when in combination with potassium or ammonium sulphate. It is unlike copper sulphate in that a single molecule of water is not sufficient to develop its full susceptibility and it requires at least $7H_2O$ to do so, whereas in the anhydrous state one molecule of potassium or ammonium sulphate will give a maximum susceptibility.

The most usual form of nickel-sulphate crystals appears to be $NiSO_4.6H_2O$. The heptahydrate was specially crystallized at a low temperature. As the hexahydrate is dimorphous, crystallizing in both square prismatic and monoclinic forms, it cannot always be easily distinguished from the rhombic heptahydrate. Some confusion may result unless the water of hydration is carefully determined.

Chromium. It appears to be very difficult to obtain anhydrous chromic sulphate, methods given in the text-books having failed to give satisfactory results. It is useless to attempt to dehydrate the hydrated salt as it loses SO_3, and a basic salt or ultimately chromic oxide results. But the double salts can be dehydrated by careful heating. Chrome alums show the highest value of susceptibility for chromium sulphate, which to a great extent is maintained in the anhydrous state. While potassium chrome alum forms a definite hydrate with $6H_2O$, ammonium chrome alum seems to be unstable at that degree of hydration.

On the whole, chromium salts show an even smaller variation than nickel sulphate under varying combinations.

Copper. Copper sulphate has been included in this examination, because although not a salt of a magnetic metal, it was one of the earliest in which the effect of hydration was studied. As the susceptibility is low the changes naturally are small, and in the case of normal copper-sulphate crystals the apparent susceptibility would be appreciably raised if the negative value of the four molecules of water of crystallization were taken into account. This modification has not been introduced into table 1 in order to maintain consistency with the results for other salts in which the diamagnetic effects of water or of potassium sulphate is of far less importance.

The highest susceptibility is given by the monohydrate, and this confirms the general results obtained by Feytis and by Gray and Birse to which reference has already been made. In the case of copper sulphate the influence of potassium and ammonium sulphates in increasing susceptibility is less than that of a single molecule of water.

Water. After measurement of the susceptibilities of copper salts with the weak suspension, a determination of the constant for water was attempted as a check on the instrument and the standard of reference. After correction for the repulsion of the diamagnetic glass tube a value of $-0{\cdot}730 \times 10^{-6}$ was found at a temperature of 18° C. This is not put forward in any way as a fresh determination for water but merely as a check on calibration: even in this respect it is not of much use as the coefficient for water has been so variously estimated, from the $-0{\cdot}689 \times 10^{-6}$ found by Jäger and S. Meyer up to $-0{\cdot}79 \times 10^{-6}$ obtained by Koenigsberger and by Curie and Cheneveau. P. Sève* in his report to the Congrès International d'Électricité in 1932 adopts the value found by Piccard and Devard of

$$-0{\cdot}71993 \times 10^{-6},$$

or as a round figure $-0{\cdot}72 \times 10^{-6}$, as being accurate to 1 in 1000.

§ 6. CONCLUSIONS

It will be seen on reference to table 1 that when potassium sulphate is substituted for the water of constitution in the sulphates of iron, cobalt and nickel, there is a distinct increase in the susceptibility of the active constituent (column 4) and of the molecular susceptibility (column 5) which frequently persists and shows its effect in the fully hydrated double salts. This effect is very small but in the same direction in the case of manganese, but with copper sulphate a single molecule of water is more effective in increasing susceptibility than a molecule of either potassium or ammonium sulphate; in fact the latter, in the anhydrous salt, appears to act as a diamagnetic substance.

§ 7. A NOTE ON THE INCREASE IN SUSCEPTIBILITY PRODUCED BY HEATING COBALT SALTS

All values of susceptibility given in what follows are in 10^{-6} c.g.s. units.

In 1925 A. Serres† discovered that cobalt sulphate after having been dehydrated at a low red heat gave a susceptibility which indicated that it had 26 magnetons instead of the 25 previously assigned to it. In the following year A. Chatillon‡ published the results of experiments on cobalt chloride and referred also to cobalt sulphate. He found 26 magnetons in the case of anhydrous cobalt chloride and in a later paper§ reviews the whole subject and states that cobalt chloride in solution has been found with 22, 23, 24 and 25 magnetons and in the anhydrous state with 26.

Chemical knowledge of the ease with which most chlorides from that of magnesium upwards are hydrolyzed or oxidized would lead one to expect some such change on heating their hydrates especially in air. It was found that when cobalt chloride was dehydrated by gradual heating in air to 130° it gave a value of 90·75 for χ, but when it was heated in air to 200°–230° values ranging from 101 to 105 were consistently obtained. These high values if referred to cobalt chloride alone would give it nearly 28 magnetons; but it was found in all cases in which this chloride showed exceptionally high susceptibility that when it was dissolved in water oxychloride was always deposited on standing, the amount of it being variable.

[*] *Science Abs.* **35**, 5249 (1932).

[†] *Comptes Rendus*, **181**, 714–15 (1925).

[‡] *Comptes Rendus*, **182**, 765 (1926).

[§] *Annales de Phys.* **9**, 187–260 (1928).

Dehydration in a vacuum produced by a mercury pump was then tried in order to exclude oxygen and to facilitate the removal of the water: this yielded an anhydrous chloride that although it had been heated to 230° gave a value of 91·2 for χ.

As it is well known that the addition of ammonium chloride to magnesium chloride prevents the hydrolysis of the latter salt on concentration and drying, the double salt $CoCl_2 . 2NH_4Cl$ was prepared and after evaporation to dryness and heating in air to 130° the double salt gave a value 40·2 for χ corresponding to 73·5 for its contained cobalt chloride. Evidently the anhydrous cobalt chloride shows no specially high susceptibility in combination with ammonium chloride. The latter salt was then expelled by heating to 350° in a vacuum and after being cooled the residual cobalt chloride showed a susceptibility of 92·5. On solution in water it gave hardly a trace of oxychloride.

It must therefore be concluded that the value of χ for anhydrous cobalt chloride practically free from oxychloride is about 91 or 92, which justifies Chatillon's number of 26 magnetons. But in cases in which oxychloride is produced the susceptibility may evidently become considerably greater.

Nickel chloride furnishes confirmatory evidence, for when dehydrated in air at 200° it gave a value of 49·2 for χ, but when the dehydration was carried out in a current of dried carbon dioxide the value obtained was 37·5. The former figure would give a magneton number of over 19 while the latter would give only a little over the accepted value of 16: but even in this case the susceptibility of the anhydrous chloride is somewhat greater than for the same salt in solution.

It was found that although cobalt sulphate is fairly stable it slowly loses SO_3 when heated in air to temperatures above 600° and a basic sulphate is formed. This is rendered evident on solution of the salt after it has been strongly heated. When dehydrated in air at above 300° it yielded values of χ ranging from 63·2 to 66·2, but after dehydration in a good vacuum with a drying-tube attached the value of 61·6 given in table 2 was obtained. This figure was raised to 62·2 after further heating to over 400° *in vacuo*.

After this salt, previously dried at 300°, had been heated to a low red heat in air, values ranging from 75·6 to 83·5 were obtained for χ. As it appeared doubtful to what extent this increase in susceptibility might be due to the production of a basic sulphate, salts of a more fixed acid were examined.

Cobalt orthophosphate, $CO_3(PO_4)_2$, and pyrophosphate, $CO_2P_2O_7$, were prepared and dehydrated at 300° and their susceptibilities were determined. At this stage the former gave a value 76·6 for χ which for one third of the molecular weight gives χ_M 0·009370; and after it had been heated to a little above 600° the value of χ_M was found to be raised to 0·01008. But after being heated this salt became somewhat darker in colour, a fact which suggests the production of a small amount of cobalt oxide, as if at the high temperature some of the orthophosphate had been converted into pyrophosphate and cobalt oxide.

Cobalt pyrophosphate however was quite stable at temperatures considerably above 600° and became a lighter blue in colour: after dehydration at 300° its value for χ was 67·3 but after it had been heated to 630° this value was raised to 81·4 which gives, for half the molecular weight, $\chi_M = 0{\cdot}01188$ c.g.s. unit, a value equivalent to 26 Weiss magnetons or rather more.

Table 2

Formula	Maximum temperature attained (°C.)	Conditions	Temperature of measurement (°C.)	χ (10^{-6} units)	χ_M (c.g.s. units)
$CoCl_2$	130	In air	17·5	90·75	0·01178
,,	230	In air	18–22	101–105	0·01684 (mean)
,,	230	*In vacuo*	18·5	91·2	0·01184
$CoCl_2 . 2NH_4Cl$	130	In air	17	40·2	0·009523
$CoCl_2$ from above	350	*In vacuo*	18	92·5	0·01201
$CoSO_4$	300	In air	17–20	63·2–66·2	0·010305 (mean)
,,	300	*In vacuo*	18	61·6	0·009549
,,	450	*In vacuo*	18	62·2	0·009642
,,	630	In air	17·8	83·5	0·01294
$Co_3(PO_4)_2$	300	In air	18	76·6	0·009370
,,	600	In air	18	82·4	0·01008
$Co_2P_2O_7$	300	In air	18·5	67·3	0·009826
,,	630	In air	18·5	81·4	0·01188
$NiCl_2$	200	In air	20	49·2	0·006376
,,	200	In dry CO_2	18	37·5	0·004857

In some of these cobalt salts therefore there appears to be a true increase in susceptibility after they have been raised to a high temperature and in others there is also a spurious effect due to the production of oxychloride or basic salts, and it is very difficult to distinguish in some cases between these effects.

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A NOTE ON DAVISSON'S ELECTRON-LENS FORMULAE

By L. H. BEDFORD

Communicated by R. A. Watson Watt, May 1, 1934.

ABSTRACT. A simple proof of the Davisson electron-lens formulae is developed, and their proper interpretation is given for the important case of a lens system with differing entrance and emergence velocities.

§ 1. INTRODUCTION

C. J. DAVISSON(1) has published in two short abstracts in the *Physical Review* the results of an investigation of the electron-lens properties of an aperture in a conducting plane separating two regions of different electric field-strengths. The case contemplated is that of a conducting plane which in the absence

$\mathbf{E}_1, \mathbf{E}_2$ of perforation has uniform electric fields $\mathbf{E}_1$ and $\mathbf{E}_2$ perpendicular to the plane on the two sides. An aperture is then made in the plane, without any other change in the system producing the fields. The aperture may take the form either of a long narrow slit (two-dimensional case) or of a circular hole (three-dimensional case). Davisson states that if the aperture is now irradiated with electrons it exhibits the properties of a thin lens of focal length given by

$$f = \frac{kV}{E_2 - E_1},$$

where

f — f is the focal length of the lens,

V — V is the velocity-voltage of the incident particles,

E_1, E_2 — E_1 and E_2 (scalars) are the magnitudes of the field-strengths on the entry and exit sides before the perforation is made, these fields being reckoned positive when they accelerate the electrons, and

k — k is a constant having a value 2 for the two-dimensional case (cylindrical lens) and 4 for the three-dimensional case (spherical lens).

The object of this note is to show how the aperture comes to possess the properties of a thin lens, to derive a proof of Davisson's formulae, and to show how the formulae should be interpreted.

Suppose that a conducting plane P separates two regions of field-strengths E_1 and E_2 and suppose that E_1 and E_2 are both positive and $E_2 > E_1$. Before the aperture is made the equipotential surfaces are planes parallel to the plane P and the lines of force are straight lines normal to it. When an aperture is made in the plane, having a size small compared with the dimensions of the system producing field, then in places remote from the aperture the field is not disturbed, but in the immediate neighbourhood of the aperture we have a transition region in which the field varies from E_1 to E_2.

A complete and extremely elegant solution for the field distribution in the neighbourhood of a circular hole has been given by T. C. Fry(2). However, the simplicity and generality of Davisson's results suggest that we do not need any such elaborate solution, but that the results must follow from general principles subject possibly to simplifying assumptions. Thus we may attempt to deduce to Davisson's formulae from the general properties of an electric field subject to an abrupt transition. Now the vector field $\mathbf{E}$ has to satisfy the condition div $\mathbf{E} = 0$ everywhere, and has to assume the values $\mathbf{E}_1$ and $\mathbf{E}_2$ on the two sides of the plane in regions remote from the aperture. Further, we shall have symmetry about the axis of the hole, or about the axial plane of the slit, in the three- and two-dimensional cases respectively. Let us represent this state of affairs by a field which has the value $\mathbf{E}_1$ up to the plane $x = 0$, a transition from $\mathbf{E}_1$ to $\mathbf{E}_2$ over the slab of space between the planes $x = 0$ and $x = a$, and has the value $\mathbf{E}_2$ for $x > a$, figure 1.

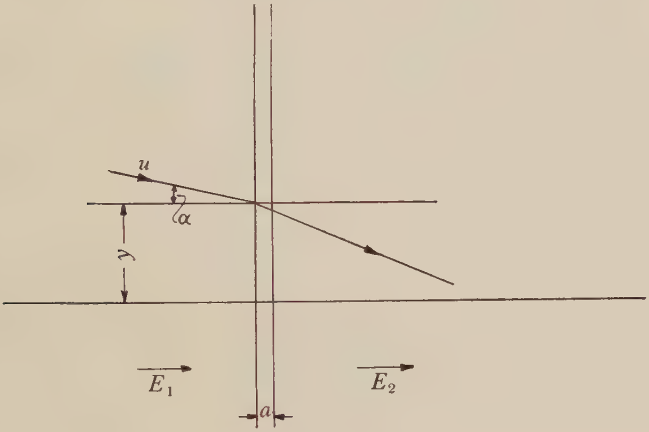

Figure 1.

§ 2. THE TWO-DIMENSIONAL CASE

Here we have to consider a long narrow slit, which has the effect of a cylindrical lens.

The condition div $\mathbf{E} = 0$ may be written

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} = 0;$$

also, since $\mathbf{E}$ is derived from a potential,

$$\frac{\partial E_y}{\partial x} = \frac{\partial E_x}{\partial y}.$$

Then

$$dE_y = \frac{\partial E_y}{\partial x}\,dx + \frac{\partial E_y}{\partial y}\,dy$$

$$= \frac{\partial E_x}{\partial y}\,dx - \frac{\partial E_x}{\partial x}\,dy.$$

If we assume $\partial E_x/\partial y = 0$, which is certainly true near the plane of symmetry,

$$dE_y = -\frac{\partial E_x}{\partial x}\,dy.$$

Assuming $\partial E_x/\partial x$ to be independent of y, which is likewise true near the plane of symmetry, we have

$$E_y = -\left(\frac{\partial E_x}{\partial x}\right)y,$$

y y being measured from the plane of symmetry.

u Now consider an electron entering the transition slab with velocity u at a distance
α y from the plane of symmetry, and moving at a small angle α to the axial direction. (This angle α and all other ray angles are assumed to be so small that it is not necessary to distinguish between the angle, its sine or its tangent. Likewise it is not necessary to distinguish numerically between the velocity u and its axial component.)
e During its travel through the slab the electron is subject to a force eE_y away from the axis, i.e. a force $e\,(\partial E_x/\partial x)\,y$ towards the axis. If we assume that the slab is so thin that the velocity u in the x direction is not appreciably altered within the slab, the time of travel through the slab will be a/u. The transverse momentum acquired is therefore

$$\int_0^a e\left(\frac{\partial E_x}{\partial x}\right)y\,\frac{dx}{u}$$

or

$$\frac{ey}{u}\,(E_2 - E_1).$$

The angular deviation of the ray is thus

$$\frac{ey}{mu^2}\,(E_2 - E_1),$$

which

$$= \frac{ey}{2eV}\,(E_2 - E_1)$$

$$= \frac{y}{2V}\,(E_2 - E_1).$$

The electron ray thus receives an angular deviation proportional to its distance from the axial plane, which is exactly the property of a thin cylindrical lens in optics. In the optical case of a cylindrical lens of focal length f the deviation of the ray is y/f; hence we see that in the electron lens

$$f = \frac{2V}{E_2 - E_1} \qquad \text{......(1).}$$

§ 3. THE THREE-DIMENSIONAL CASE

In this case we have a circular hole acting as a spherical lens. The condition div $\mathbf{E} = 0$ may now be expressed in cylindrical polar co-ordinates in the form

$$\frac{\partial E_x}{\partial x} + \frac{1}{r}\frac{\partial}{\partial r}(rE_r) = 0,$$

where r is measured from the axis of symmetry. On account of symmetry the third co-ordinate θ does not appear; $E_\theta = 0$. Also, since $\mathbf{E}$ is derived from a potential, r

$$\frac{\partial}{\partial x}(rE_r) = r\frac{\partial E_x}{\partial r}.$$

Then
$$d(rE_r) = \frac{\partial}{\partial x}(rE_r)\,dx + \frac{\partial}{\partial r}(rE_r)\,dr$$

$$= r\frac{\partial E_x}{\partial r}\,dx - r\frac{\partial E_x}{\partial x}\,dr.$$

If we assume E_x to be independent of r (when x is constant),

$$d(rE_r) = -r\frac{\partial E_x}{\partial r}.$$

Assuming $\partial E_x/\partial x$ to be independent of r,

$$rE_r = -\frac{r^2}{2}\frac{\partial E_x}{\partial x},$$

$$E_r = -\frac{r}{2}\frac{\partial E_x}{\partial x}.$$

Hence, proceeding as before, we find that the circular hole is analogous to a thin spherical lens and has a focal length

$$f = \frac{4V}{E_2 - E_1}.$$

§ 4. EFFECT OF CHANGE OF VELOCITY

In deriving the above results we have assumed that the transition zone is extremely short, so short in fact that the ray emerges with sensibly the same velocity-voltage as that with which it entered. Now in most practical applications this is not the case, and we therefore require to know how to interpret the Davisson formulae when the velocity of emergence differs from that of the entrance. This case will be illustrated in terms of a simple example, that of the double-disc accelerating lens. This example not only is itself very important in practice, but also is in a sense typical of all the practically important forms of electron lens. A double-disc lens, depicted in figure 2, consists of two circularly perforated discs separated by a distance d with the holes aligned on a common normal; electrons enter from one side with d

V_1, V_2 E_{12} E_1 E_2

a velocity-voltage V_1 and are accelerated between the discs to a velocity-voltage V_2. Between the discs and "before the holes are drilled" there exists a field E_{12} equal to $(V_2 - V_1)/d$. On the entrance side we may assume a smaller field E_1 and on the exit side a field E_2, usually zero. Davisson's formula tells us that the first hole represents a lens of focal length f_1, where

$$f_1 = \frac{4V_1}{E_{12} - E_1}.$$

f_1, r

The meaning of this focal length f_1 is that a parallel ray entering at a distance r from the axis is deviated inwards through an angle r/f_1. This deviation is supposed to take place abruptly in the plane of the first disc. Thereafter the electrons pass through a sensibly uniform accelerating field whereby the axial velocity is increased in the ratio $\sqrt{(V_2/V_1)}$; consequently the inclination to the axis is reduced by this ratio and the angle at which it enters the second disc is $\sqrt{(V_1/V_2)}\,r/f_1$. At the second disc a further deviation occurs, and since $E_{12} > E_2$ this deviation is outwards; that is to say the second disc acts as a diverging lens. The angle through which the ray is bent at the second disc is r/f_2, where $f_2 = 4V_2/(E_2 - E_{12})$, a negative quantity. Hence, due regard being paid to signs, the final inclination of the ray on leaving the second disc is $\sqrt{(V_1/V_2)}\,r/f_1 + r/f_2$, and the total focal length of the combination is

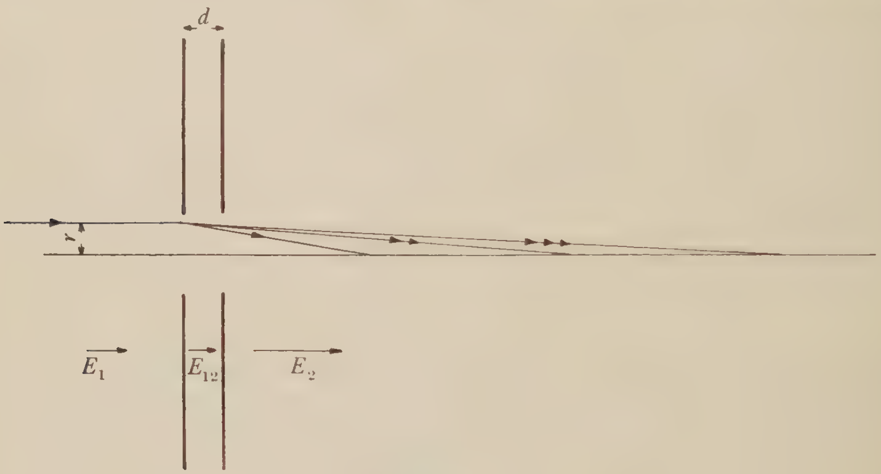

Figure 2.

f_2

$$\frac{1}{\frac{1}{f_1}\sqrt{\left(\frac{V_1}{V_2}\right)} + \frac{1}{f_2}} \qquad \text{......(2).}$$

In this form, however, the result is not of immediate importance because the ordinary geometrical construction for image and object does not apply; this is because, on account of the increase of axial velocity between the two discs, a centric ray is not undeviated.

In order to be able to apply the usual lens construction, which is particularly significant for the reckoning of the magnification, we may envisage the effect of the increase of velocity as a compression of the scale of axial distance. Figures 3 and 4 make this clear.

In figure 3 is shown the actual state of affairs. The distance f is that given by the expression (2) above. In figure 4 the axial distances on the emergence side of the lens have been divided by the factor $\sqrt{(V_2/V_1)}$; the centric ray is now undeviated and the ordinary construction applies. The (focal length) f' in this figure is

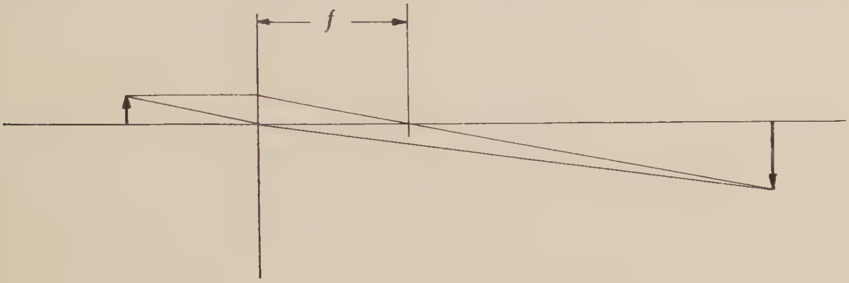

Figure 3.

$$\frac{1}{\sqrt{\left(\frac{V_2}{V_1}\right)}}\cdot\frac{1}{\frac{1}{f_1}\sqrt{\left(\frac{V_1}{V_2}\right)}+\frac{1}{f_2}}, \quad \text{or} \quad \frac{1}{\frac{1}{f_1}+\frac{1}{f_2}\sqrt{\left(\frac{V_2}{V_1}\right)}},$$

or

$$\frac{1}{\frac{1}{f_1}+\frac{1}{f_2'}},$$

where $f_2' = f_2\sqrt{(V_1/V_2)}$.

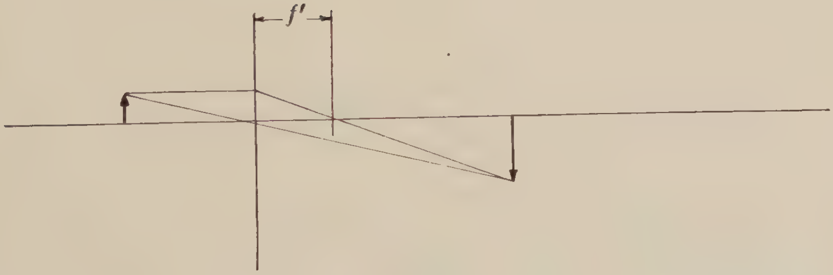

Figure 4.

This form of representation reminds us of the analogous optical case of a lens separating media of different refractive indices. The magnification reckoned in this way agrees with that found by von Ardenne(3).

We may now work out the important case of the double-disc lens in which there is no field on either side of the lens but only the field $(V_2 - V_1)/d$ between the discs.

We then have

$$f_1 = \frac{4V_1 d}{V_2 - V_1},$$

$$f_2 = -\frac{4V_2 d}{V_2 - V_1},$$

$$f_2' = -\frac{4\sqrt{(V_1 V_2)}\, d}{V_2 - V_1},$$

$$\frac{1}{f'} = \frac{V_2 - V_1}{4V_1 d} - \frac{V_2 - V_1}{4\sqrt{(V_1 V_2)}\, d}$$

$$= \frac{V_2 - V_1}{4d} \cdot \frac{1}{V_1} \left\{1 - \sqrt{\left(\frac{V_1}{V_2}\right)}\right\},$$

$$f' = \frac{4V_1 d}{V_2 - V_1} \cdot \frac{1}{1 - \sqrt{(V_1/V_2)}}.$$

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535·317

IMAGE-DISTORTION DUE TO GLASS-THICKNESS IN LENS SYSTEMS. PART 2

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of the Taylor-Hobson Research Department

Communicated by William Taylor, F.R.S., February 28, 1934, *and in revised form June* 3, 1934.

ABSTRACT. The simplest method of applying the formulae given in part 1* is discussed. The formulae are applied to a Series V Cooke lens of 10-in. equivalent focal length. The effects of the three axial glass-thicknesses in producing fractional distortion in the final image or focal plane are ascertained by the application of two alternative but mutually confirming methods, the older and simpler of which is recommended for adoption.

My purpose in this second paper is to show that the correct procedure for arriving at the fractional distortion carried forward to the final image plane of a system of coaxial lenses and corresponding to any oblique principal ray traversing a parallel glass plate, is to work out first the fractional distortion produced by each parallel plate in its own second conjugate image plane. The algebraic sum of the several fractional distortions of all the parallel glass plates implied in the lens-thicknesses, together with the fractional distortions produced by all the lens elements, should vanish if the whole lens combination is to be rectilinear.

The theorem as stated in my *System of Applied Optics*, upon which the above method of summation rests, is that not only each lens element but each parallel plate also in its turn copies or carries forward to its second conjugate image plane any fractional distortional error existing in the second conjugate image planes of the preceding lens elements and parallel plates, at the same time adding its own fractional distortional error to those of all the preceding lens elements and parallel plates.

As, however, I began to feel some doubt regarding the validity, when the distortions arising in a lens system are summed up, of treating the distortions produced by parallel plates in exactly the same way as the distortions produced by the lens elements, I decided as a test to transfer the distortion effects of each parallel plate to the final focal plane by another method, as explained below, and find whether it justified the above-defined simpler method of summation as applied not only to the principal rays which are *angularly* deviated by the lens elements but also to the same principal rays when they are *side-stepped* by their passage through each of the parallel plates.

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* *Proc. Phys. Soc.* **46**, 283 (1934).

It is of course assumed at the outset that the image fields of all the simple lens elements and parallel glass plates involved in the lens combination to be dealt with are flat, according to the first-order or Gaussian assumption. If curvature of the image fields were to be taken into account, the resulting fractional distortion formulae would involve functions of $\tan^4 \chi$, $\tan^6 \chi$, etc., thus becoming formulae of higher orders.

Figure 1 is a section of the 10-in. E.F.L. Series V Cooke lens, which is utilized as an example for the application of the formulae numbers (1) to (3) of part 1 of this paper*. The specification of the glasses with radii of curves, axial lens-thicknesses and air spaces in inches is as follows.

L_1 and L_3 are of densest baryta crown glass with μD equal to 1·6114.

L_2 is of extra light flint glass with μD equal to 1·5482.

Radii	Axial thicknesses	Air spaces	Focal lengths of elements
L_1 $\begin{cases} r_1 = 1{\cdot}457 \\ r_2 = 10{\cdot}013 \end{cases}$	0·299		$f_1 =$ 2·38 $f_2 =$ 16·56
		0·038	
L_2 $\begin{cases} r_3 = -5{\cdot}593 \\ r_4 = -1{\cdot}327 \end{cases}$	0·046		$f_3 = -$ 10·2 $f_4 = -$ 2·42
		0·895	
L_3 $\begin{cases} r_5 = 101{\cdot}2 \\ r_6 = 6{\cdot}975 \end{cases}$	0·183		$f_5 =$ 165 $f_6 =$ 11·41

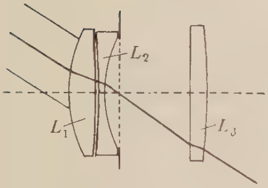

Figure 1.

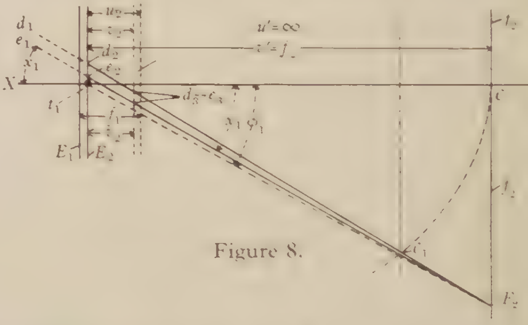

Figure 8.

In figure 8† E_1 and E_2 are the two elements enclosing the first parallel plate and $e_1\,e_2$ is the principal ray (AA_1 of figure 3) which after refraction through the first element E_1 is refracted through the enclosed parallel plate and emerges from the latter lifted to the position $d_1\,d_2$. It is then converged by the element E_2 to the oblique focus F_2 in its principal focal plane.

It should be noted here that I have assumed the rays of pencils entering the first element E_1 of the system on the left (shown dotted) to be parallel as if proceeding from a very distant object, and in figure 3 the dotted entering ray D_2 passes through the centre of the first lens element $E_1 \ldots E_1$ without deviation, making an angle of 27° 39′ with the optic axis.

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* *Loc. cit.*

† The numbering of the figures in part 1 has been retained in the present paper for convenience of references.

Then we have the condition that the ray $e_1 e_2$, figure 8, after emergence from the plate is lifted parallel to itself, thus becoming ray $d_1 d_2$, and the next problem is to find a formula which will define the effect of this lift in the *final focal plane* of the three-lens combination of figures 1 and 2.

Should it be required to allow for the curvature of the image field of E_2, shown dotted, then the real oblique focus may be at or towards C_1, but the formulae required to correct for such curvature of image deviations of the second, third, fourth, fifth and sixth elements would be expressed by smaller corrections of the next higher orders, in the shape of formula (2) or (3) of my last paper multiplied by a function of f_2^{-1} ($\tan^2 \phi_2$), f_3^{-1} ($\tan^2 \phi_3$), etc., resulting in corrections of higher orders $\tan^4 \chi$, $\tan^6 \chi$, etc., only required when exceptional accuracy is wanted, so that we may legitimately assume the images formed by pencils of parallel rays at the principal focal distances of the second, fourth and sixth elements also to be flat.

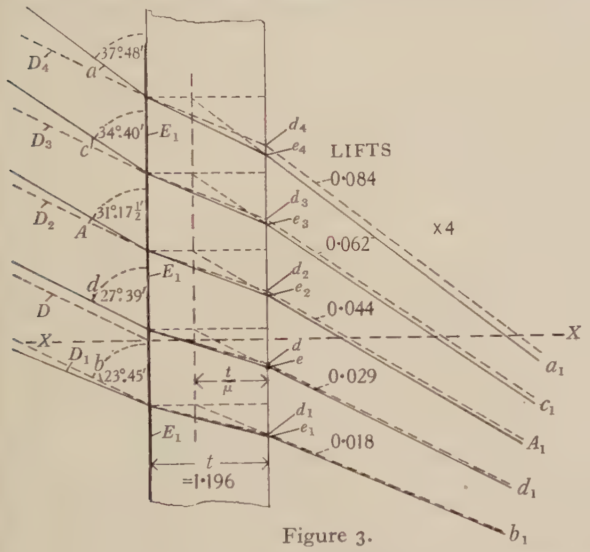

Figure 3.

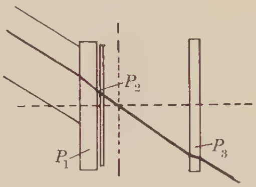

Figure 2.

But figures 8 and 10 suggest that the curvatures of image fields of some of the several elements may be considerable, besides increasing at an accelerating pace after angles of obliquity of about 30° have been reached. Thus the distortions of the next higher order due to such curvatures of image fields may become too serious to be neglected consistently with rectilinear projection and clear enough definition throughout the fields of view, in the case of photographic and projector lenses designed to give a half field of view of 35° or more. It should, moreover, be borne in mind that the curvature-of-field corrections of the six lens elements and three plates are balanced off against each other, in order to secure the final flat field.

Returning to the question of the effect in the final image plane of the distortion brought about by the first parallel plate involved in the first lens, illustrated in figure 8, we may note that the vertical lift $e_2 d_2$ of the principal ray $e_1 e_2$, figures 3 and 8, in this case is only 0·011 in.* and the hypothetical ray $e_1 e_2$ and the real lifted ray $d_1 d_2$ must be considered to focus or intercross at F_2 in the principal focal plane of E_2, which is 16·53 in. behind e_2. Clearly the projection angle between the two rays after refraction by E_2 is $(e_2 \dots d_2)/f_2$ or 0·011/16·53 (in which f_2 is constantly expressed as its axial value $E_2 \dots c$ and not $E_2 \dots F_2$); this projection angle will become modified by each successive refraction through the remaining four elements. Therefore a formula is required for expressing the distortional effect of the original lift $e_2 \dots d_2$, when transferred to the final focal plane.

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* The lifts in figure 3 are four times exaggerated.

u_2, v_2 As u_2 and v_2 have so far designated the axial distances from E_2 of its two conjugate focal planes (−2·1975 and 1·9405 in the present case), then we may conveniently use the accented symbols u_2' and v_2' to designate the axial distances from E_2 of its conjugate focal planes when the rays e_1 and d_1 enter the element E_2 parallel, as in figure 8, so that $u_2' = \infty$ and $v_2' = f_2$.

u_2', v_2'

It should be noted here that what I have named a "projection angle" is in itself a very inconstant quantity, as is explained by figure 12. It is clear that if $A_1 \dots A_2$ is the optic axis, C the centre of a lens element, and $a_2 \dots b_2$ a radial displacement in the first conjugate flat image $A_1 \dots a_2$ presented to lens element C, then the projection of $a_2 \dots b_2$ on to the second conjugate focal plane of C will become

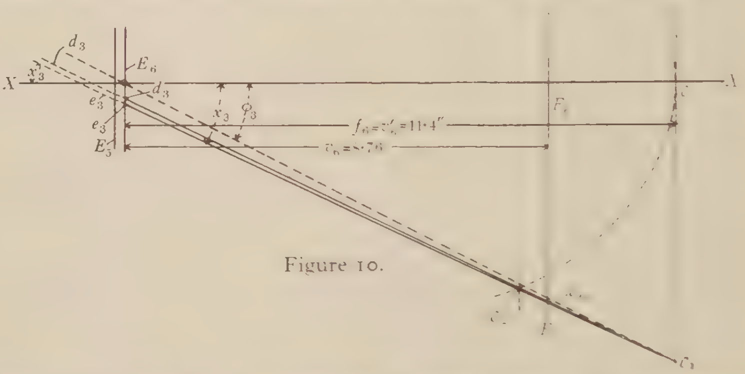

Figure 10.

$$a_2 \dots b_2 \times C \dots A_2/A_1 \dots C \quad \text{or} \quad a_2 \dots b_2 \times v/u \quad \text{or} \quad a_2' \dots b_2',$$

while $a \dots b \times v/u = a' \dots b'$ and so on. This first-order relationship holds good

, χ_2, χ_3 whatever the angles of obliquity χ_1, χ_2 and χ_3 may be, although the projection angles

, ϕ_2, ϕ_3 ϕ_1, ϕ_2 and ϕ_3 can be proved to diminish in proportion to $\cos^2 \chi$. Thus the factor $\cos^2 \chi$ can be ignored when radial displacements are transferred from the first conjugate focal plane of a lens element to their images in its second conjugate focal plane.

Then it is clear that the two rays converging to F_2, figure 8, embrace a projection angle which is $e_1 \dots d_1/f_2$ or 0·011/16·56 to start with. Similarly we may designate the

l_1, l_2, l_3 vertical parallel lifts initially produced in the three parallel plates as l_1, l_2 and l_3 respectively.

So the above angle starts as l_1/f_2 after refraction by E_2; this angle, enclosed between the two rays, becomes modified at each successive refraction by the following elements E_3, E_4, E_5 and E_6, and a formula is required to express the linear amount of vertical displacement, towards or away from the optic axis, resulting when each of the two rays at last intersects the final focal plane to the right of E_6.

In this case the vertical displacement in the final focal plane, caused by the first parallel plate, is

$$\frac{l_1}{f_2}\left(\frac{u_3'\, u_4'\, u_5'\, u_6'}{v_3'\, v_4'\, v_5'\, v_6'}\right)(v_6' + \text{b.f.l.}) \text{ or } E_1,$$

in which b.f.l. is the back focal length or the distance v_6 from E_6 to the final image plane. b.f.l.

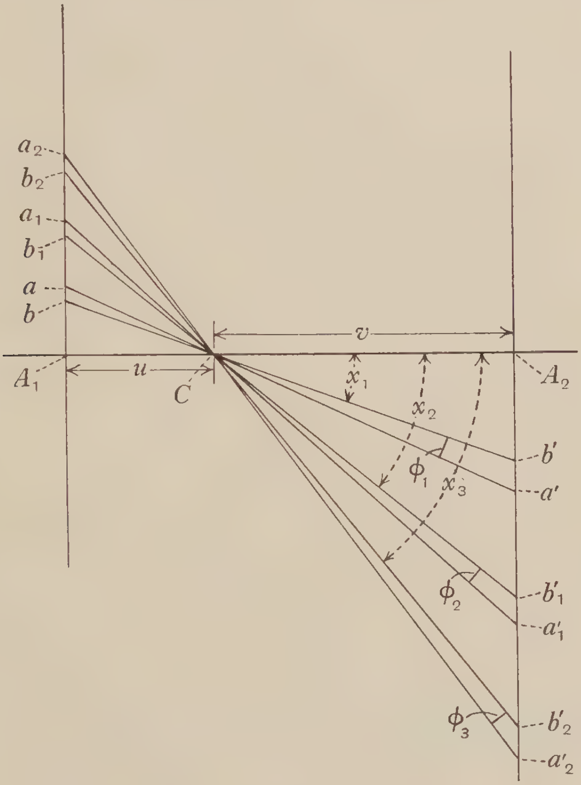

Figure 12.

After the u's and v's have been ascertained, this formula becomes

$$\frac{-0{\cdot}01095}{16{\cdot}654}\left(\frac{16{\cdot}526 \times 26{\cdot}68 \times 3{\cdot}114 \times 3{\cdot}288}{26{\cdot}65 \times 2{\cdot}219 \times 3{\cdot}172 \times 4{\cdot}62}\right)(4{\cdot}62 + 8{\cdot}758),$$

which $= (-0{\cdot}01095)\,(0{\cdot}3146)\,(13{\cdot}378) = -\,0{\cdot}046$ in.

of linear radial distortion in the principal focal plane of the 10-in. E.F.L. Cooke lens, or about $\frac{1}{20}$ in. of inward displacement from the correct position.

The fractional distortion produced by the first parallel plate is

$$\frac{-\,0{\cdot}0461}{10'' \tan 27^\circ} = \frac{-\,0{\cdot}0461}{5{\cdot}096} = -\,0{\cdot}00905 \qquad \text{......(D)},$$

which, in angular value, is about 24′, or $\frac{4}{5}$ of the angular diameter of the full moon. This, in itself, would be a very serious amount of distortion in a photographic lens designed to give strictly rectilinear images.

It should be noted that figure 8 does not attempt to show the further course of the two rays $e_1 e_2$ and $d_1 d_2$ through the four following elements on their way to the final focal plane; otherwise the diagram would be undesirably complicated. But figures 9 and 10 show the simpler course of the rays resulting from the lifts l_2 and l_3 produced by the parallel plates enclosed in the second and third lenses of the combination shown in figure 1.

The case of the negative lens L_2, figure 1, is illustrated in figure 9. Its centre thickness is only 0·046 in. and the appropriate formula is

$$\frac{l_2}{f_4}\left(\frac{u_5'\ u_6'}{v_5'\ v_6'}\right)(v_6' + \text{b.f.l.}), \text{ or } E_2.$$

The angle of obliquity χ_2 here $= 31^\circ\ 12'$ and the lift $l_2 = 0{\cdot}00107$ in., so the formula in figures is

$$\frac{-0{\cdot}00107}{2{\cdot}4205}\left(\frac{3{\cdot}316 \times 3{\cdot}5}{3{\cdot}383 \times 5{\cdot}04}\right)(5{\cdot}04 + 8{\cdot}758).$$

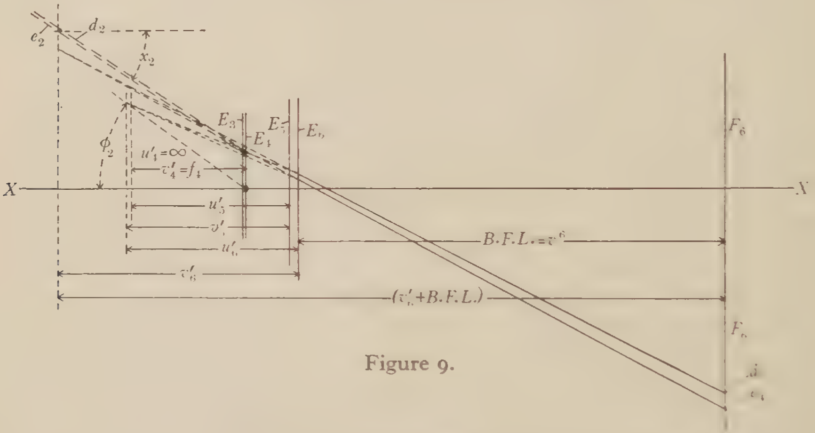

Figure 9.

This gives $-0{\cdot}00415$ as the negative linear displacement in the final focal plane, or four times the original lift l_2. The proportional distortion resulting from l_2 is

$$\frac{-0{\cdot}00415}{10''\tan 27^\circ} \text{ or } \frac{-0{\cdot}00415}{5{\cdot}096} \text{ or } -0{\cdot}0008,$$

corresponding to $-2'$ only.

The parallel plate of the third lens yields a linear distortion E_3 expressed by

$$l_3(f_6 - v_6)/f_6 \text{ which} = -0{\cdot}0056(11{\cdot}41 - 8{\cdot}76)/11{\cdot}41 = -0{\cdot}0013 \text{ in.}$$

But $-0{\cdot}0013/10''\tan 27^\circ = -0{\cdot}00026$, corresponding to about $\frac{1}{2}'$, so the effect here is negligible.

This last case is illustrated in figure 10, in which E_5 and E_6 are the two element planes of the third lens, enclosing between them the third parallel glass plate, while $c \ldots c_1$ is the principal focal plane of E_6, and $c \ldots c_2$ is the curvature of its field (probably exaggerated). Then e_3 and d_3 are the original and lifted rays, respectively, entering E_6 parallel and then refracted to c_1 in the principal focal plane of E_6. But if the curved field (dotted) of E_6 is taken into account it is clear that the rays d_3 and e_3

will intercross at c_2 and then diverge again onto the final focal plane, f.f.p., at c_3 so that the linear distortion will be reversed in sign and become positive, although its amount will be still more negligible.

Thus the total distortion for all three parallel plates amounts to $-27\frac{1}{2}'$ at 27° 39′ from the centre of the field, an amount of distortion which, were it not approximately neutralized by a positive balance of the other distortions brought about by the six lens elements, would be scarcely tolerable in any photographic lens claiming to be rectilinear.

Now we are in a position to see whether this special method of translating the parallel lift of the principal ray $e_1 \ldots e_2$, caused by the first parallel plate, to its fractional distortional effect in the final image plane confirms the simpler and more convenient copying-through theorem, defined at the commencement of this paper.

We found that the exact or trigonometrical value of the lift occurring in the first parallel plate (enlarged four times in figure 3 for the sake of clearness) was 0·011 in., causing a fractional distortion in the final image of − 0·00905 as worked out by the more elaborate testing method herein used.

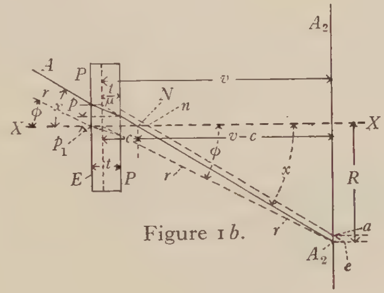

Figure 1 *b*.

Now figure 1 *b* illustrates the simpler copying-through method, and its formula in this case expresses the fractional distortion in the field of the first element E caused by the lift of the principal ray consequent on traversing the first parallel plate. The formula takes the shape

$$\frac{\text{Trigonometrical value of lift}}{(v-c)\tan\chi}$$

(see figure 1 *b*), where v, the principal focal length of the first element, = 2·38 in. and c, figure 1 *b*, is the axial distance (about 0·38 in. behind $E \ldots P$) at which the principal ray $A \ldots A_1$ in figure 3, or $A \ldots A_2$ in figure 1 *b*, crosses the optic axis after being refracted by the first lens element $E \ldots P$. The original beam of parallel rays D, D_1, D_2, D_3 and D_4, shown dotted in figure 3, enters the first lens element at an angle of 27° 39′ to the perpendicular, or to the optic axis $X \ldots X$. The ray D_2 after refraction by the first lens element E_1 then takes the direction indicated by the full line above D_2 to the left of the first element $E_1 \ldots E_1$ and then enters and leaves the parallel plate, making an angle of 31° 17½′ with the optic axis $X \ldots X$. The refraction by the first element has thus changed the original 27° 39′ of obliquity to 31° 17½′. We have seen that the essential algebraic formula for expressing the fractional or proportional distortion in the image plane projected by the element E_1 through the parallel plate is

$$\frac{\text{Vertical lift of ray } A \dots A_2}{(v - c) \tan \chi}$$

as illustrated in figure 1 *b*, where the vertical lift

$$= t \left\{ \frac{\mu^2 - 1}{2\mu^3} \tan^3 \chi - \frac{3(\mu^2 - 1)^2}{8\mu^5} \tan^5 \chi + \text{etc.} \right\}$$

and the fractional distortion is therefore

$$\frac{t}{v - c} \left\{ \frac{\mu^2 - 1}{2\mu^3} \tan^2 \chi - \frac{3(\mu^2 - 1)^2}{8\mu^5} \tan^4 \chi + \text{etc.} \right\}.$$

For the sake of clearness we have indicated in figure 3 four times the correct lift imparted to the principal oblique ray $A \dots A_1$. For the 0·044 in. shown is four times the trigonometrically calculated value, and should be 0·011 in. so that 0·011 in. supersedes in this case the algebraic series of terms in the upper line of the last formula. This expression becomes − 0·011 (2·38 − 0·28) tan 31° 17½′, which is the same result as (D) previously obtained by the more complex method. The fractional distortion is − 0·011/2 (0·6078) or − 0·00905, so that the fractional distortion produced by the first parallel plate in the image projected through it by the first element has been exactly copied through to the final focal plane of the lens combination.

Therefore the more simple and convenient copying-through theorem holds good for the fractional distortions of the parallel plates as well as for the lens elements.

AWARD OF THE DUDDELL MEDAL, 1934, TO HAROLD DENNIS TAYLOR, F.R.S.

Address delivered by Prof. A. O. Rankine, F.R.S., President, March 16, 1934.

THE Council of this Society announced in December 1933 the Award of the Duddell Medal to Harold Dennis Taylor. It is now my very pleasant duty on behalf of the Society to present this medal to him.

This is by the regulations awarded to persons who have contributed to the advancement of knowledge by the invention or design of scientific instruments, or by the discovery of materials used in their construction. So soon after the amalgamation of the Optical Society with the Physical Society of London to form the Physical Society it is a happy coincidence that, on this occasion, the recipient should be a very distinguished investigator in the field of optics.

Mr Taylor has lived and worked in a period of the first importance in the development of optical instruments. A few investigators, notably W. Vernon Harcourt, had realized during the last century the nature of the principal problems to be solved, and might have been successful had it been possible then to manufacture the necessary types of glass. When the new Jena glasses became available for general use forty years ago, Dennis Taylor was ready to seize upon and make splendid use of the opportunities thus afforded. At that time he was the Optical Manager of Thomas Cooke and Sons of York, a firm justly celebrated for its astronomical and surveying instruments. Large astronomical refractors suffered at that period from a serious defect, known as the "secondary spectrum", which remained when the normal conditions for the removal of chromatic aberration had been satisfied. The Jena glasses provided the means for the practical elimination of this defect, and the first opportunities of using them for this purpose naturally fell to Abbe and his co-workers, who produced some apochromatic telescopic doublets. Taylor resorted to a different solution. He employed three glasses, and with rare skill and insight devised an objective in which much more than the pure optical problem was solved. Telescopes constructed to this design of Taylor's, the first triple apochromats, have met with great success. Their colour correction is so good, and is so successfully combined with the other five corrections needed, that the same instrument may be used both for visual and for photographic work. They are correctly described by their name, "photo-visual objectives." Moreover, Taylor has been more fortunate in his design than Abbe. The former used glasses of moderate, the latter of extreme properties. These extreme glasses proved to be unstable, so that instruments incorporating them deteriorated rapidly, while several of Taylor's 12-in. refractors remain still in regular use.

I turn to Dennis Taylor's next great invention, the one with which his name will always be most closely associated. In 1893 he took out two patents for photographic lenses which were later put on the market and became justly celebrated all over the world as "Cooke lenses." Their production was placed in the hands of Messrs Taylor, Taylor and Hobson of Leicester, of which firm it should be said that they manufactured the lenses so carefully and accurately that the user really enjoyed in his camera the qualities attainable from their design.

It is impossible here to discuss in detail the principles on which the lenses are constructed or even to convey an adequate idea of the beauty of the design ultimately reached. The specifications of the lenses are notable documents of high scientific value, and their importance may be judged from the fact that four official editions of them have appeared, the last nearly forty years after the patent was granted. These lenses showed how fully Dennis Taylor was master of the theory of the aberrations of lenses. In the specifications of the Cooke lenses nothing is more striking than the treatment of the theory which leads to the method of eliminating coma simultaneously with curvature and astigmatism.

If any further tribute were needed for the great qualities of these lenses, it would be afforded by the way in which they have been imitated in other lands since the expiry of the master patents, and not least by the adoption of Taylor's design for the very large photographic lenses made in Germany during the War for aerial photography.

In later years Mr Taylor has not lost the skill he displayed in his earlier inventions. Special mention should be made of the telescope in which he showed how it is possible to combine a large aperture and a large field of vision with freedom from aberrations comparable with that attained in the Cooke lenses. This is an achievement of the first order.

Optical instruments of the highest quality are no less essential for the progress of most experimental sciences than they are for many of the arts. Telescopes large and small and photographic lenses are among the indispensable tools of the physicist. The optical work of Mr Taylor places him indisputably in the front rank of those whose labours have served the advancement of knowledge. His work has been of such outstanding quality as richly to merit the recognition which the award of the Duddell Medal signifies.

Mr Dennis Taylor, in the name of the Physical Society, I ask your acceptance of the eleventh Duddell Medal and Certificate, at the same time expressing the hope that you will live long to make still more smooth the paths of scientific investigators.

GUTHRIE CENTENARY

Address delivered by Prof. A. O. Rankine, F.R.S., President, October 20, 1933.

FREDERICK GUTHRIE was born on October 13, 1833. To-day is the first meeting of the Physical Society following the centenary of his birth, and I have been asked by the Council to make a few remarks on the man and his work, as it is not proposed to celebrate the occasion in any more elaborate manner. We already remember Guthrie at least once a year in the institution of the Guthrie Lecture. The first of these annual discourses was given in 1915 by Prof. R. W. Wood, and I understand that reminiscences of Guthrie were given then, although owing to an unfortunate oversight neither these nor the lecture were published. But we are not without records in our *Proceedings*, and recently I have perused them with great interest. We have first the memoir by Prof. Carey Foster, shortly after Guthrie's untimely death in 1886, appearing on page 9 of the *Proceedings* of the session 1886–7. Then most of us had the pleasure also, during our Jubilee Celebrations in 1924, of hearing tributes to Guthrie from the lips of such men as Sir William Barrett, Sir Ambrose Fleming, Prof. Boys, Prof. Armstrong and Sir Oliver Lodge, all of whom had known our founder personally. I take this opportunity of referring you again to the record published in the special Jubilee number of the *Proceedings*, because it is impossible for me, belonging, as I do, to a younger generation, to add anything really pertinent.

What struck me most were some words of Carey Foster which I shall quote. He said "It is seldom that a scientific Society owes its existence so distinctly to the action of one man as the Physical Society of London owes its origin to the action of Frederick Guthrie." That is the principal reason why our Society honours him. He was a good physicist, and the better, according to Prof. Armstrong, for having been first a chemist and remaining one at heart all his life. As a teacher he was in the first rank, indeed a pioneer in the development of the practical side, as might have been expected from his devotion to experiment. But it is not primarily on these grounds, or even for his notable contributions to knowledge, that we mark the centenary of his birth. It is because of the unselfish zeal with which sixty years ago, in spite of some opposition and discouragement, he gathered together the nucleus of our Society, and promoted its interests ardently until he died. No one can doubt that the splendid growth in numbers and usefulness has fully justified Guthrie's aims, and we count ourselves happy to be able to continue to build upon the foundation which he laid.

There are no rival claimants, and I ask you to stand with me for a few moments as a token of our heartfelt esteem and remembrance of Guthrie, the founder of our Society.

OBITUARY NOTICES

PROF. A. P. CHATTOCK, F.R.S.

THROUGH the death of Emeritus Professor Arthur Prince Chattock, M.I.E.E., D.Sc., F.R.S., on 1st July last in his 74th year, the Society has lost an old Life Member who first joined it in 1884.

Temperamentally very self-effacing and modest, he was personally unacquainted with most of the Fellows, but those who knew him intimately or followed the record of his work in detail recognized him to be an experimenter of the first rank and a pioneer in every field that he entered. In the early eighties of last century he was investigating the possibilities of human flight and measuring the resistance offered to rotating vanes. His experiments and calculations led him to the conclusion that flight was impracticable unless some substitute for a steam engine as motive power could be found. The year 1887 found him at Liverpool insisting, before the discoveries of Hertz, as Sir Oliver Lodge relates, that the oscillatory discharges of a Leyden jar then under investigation by the latter ought to be accompanied by electric waves. A perusal of an early note-book of his, dated 1890, has recently shown that behind his well-known experiments on point discharge was an attempt to determine the ratio of the mass of an atom to its charge. The attempt was unsuccessful at the time, though he collects in his book the evidence that it gave him of the constancy of the atomic charge. In a paper on the energy of the Amperian molecule, which he published jointly with F. B. Fawcett in 1894, he was led to conclude that if magnetism had its origin in rotating electric charges this rotation was not necessarily associated with the rotation of the molecule as a whole. The discovery of the electron a year or so later filled the gap in the picture. His last important work in pure physics was also in the field of magnetism, when he made his classical determination with L. F. Bates of the gyro-magnetic ratio for iron in 1923. This was a marked experimental achievement, the final accuracy within 1 per cent being many times greater than that of any previous experimenters.

To watch him work was to realize that he had the hands of a true experimenter and a real mechanical sense. This was shown in the design of several instruments. He was one of the earliest to apply extensively the principle of measuring small forces by balancing them against a tilt. He used a high-potential electrostatic voltmeter of this design in 1891* and again applied it in the same paper to measure the field at the surface of a discharging point. It was also an important principle in several gauges that he used in his work on the pressure of the electric wind, which culminated finally in the Chattock-Fry gauge originally designed for Stanton's work on the pressure of wind on buildings†. It was this instrument, by far the most sensitive that was available at the time, which first enabled an insight to be obtained into the way in which the normal pressure varies over the surfaces of aeroplane wings and stream-line bodies. It also made possible the first accurate calibration in this country of the standard Pitot static tube, a determination to which all subsequent air-speed measurements have been referred. Another ingenious instrument, which he sometimes jocularly referred to as the best thing he had ever done, was a magnetic potentiometer devised in 1887*. This device has recently been resuscitated for use by Bates† and also by C. D. Ellis.

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* *Phil. Mag.* **32** (1891).

† *Proc. Inst. C.E.* **186**.

During a period of retirement into country life he carried out a comparison of the humidity, air flow and other physical conditions under a sitting hen and in an incubator. His paper on this subject‡ gives several illustrations of his experimental skill, for he had to devise apparatus which would not in any way disturb the hen, any bodily movement of which would have vitiated the results.

He was originally trained at University College, London in electrical engineering under Alexander Kennedy, and in physics under Carey Foster, 1879–84. Throughout the greater part of his academic career he was associated with the Physics Laboratory at Bristol, first as a demonstrator 1885–87, then as Lecturer and Professor 1889–1910, and finally as Emeritus Professor and Research Fellow 1919–24. He received the honorary degree of D.Sc. of that University in 1911, and was elected a Fellow of the Royal Society in 1921. Shortly before his final illness the Council of the University decided to create a permanent Chattock Research Studentship in Physics in recognition of his invaluable services.

Until his retirement from the Chair in 1910, the students at Bristol were fortunate in possessing a teacher of outstanding ability, whether in the lecture room or the laboratory, and one who made many great sacrifices in their interests. To those who were at one time young research students under him his inspiration, personal example, and generous friendship will remain a vivid memory.

A. M. TYNDALL

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* *Phil. Mag.* **24**.
† *Proc. Phys. Soc.* **45**, 425 (1933).
‡ *Phil. Trans.* B, **213** (1925).

SIR W. B. HARDY

Sir W. B. Hardy died on January 25, 1934. It is unnecessary here to comment on the many characteristics of his engaging personality, his breeziness, his energy, or his great versatility. This has been done adequately elsewhere, but it is proposed in this short note to indicate some of his contributions to physical science. Mention must be made of Hardy's pioneer work on colloids. He was the first to point out the importance of the electric charge on the particles as a factor in preventing their adherence and hence their coagulation, the latter taking place when the charge is nearly removed. The word "pioneer" may with justice be applied to his work on the spreading of films on water. In two papers presented to the Royal Society in 1912 and 1913 on the spreading of various substances on the surface of water Hardy suggested that the arrangement of the molecules of a pure liquid might be different at the surface from the random distribution in the interior, and suggested that if the force-field about a molecule is not symmetrical then the inwardly-directed attraction along the normal to the surface would cause orientation of the molecules there. He visualized the surface film as having a characteristic molecular architecture, the condition of minimum potential involving two terms, one relating to the variation in density and the other to the orientation of the fields of force. Another paper of considerable originality was on "the application of the principle of dynamical similitude to molecular physics." The principle was applied to the internal latent heat of evaporation of a liquid, and subject to certain assumptions it was shown that the potential energy of the repulsive forces acting between the molecules contributes to the process of evaporation.

In the Guthrie Lecture delivered before the Physical Society in 1916 Hardy discussed the physical aspects of certain phenomena of living matter.

In conclusion, mention must be made of Hardy's work on static friction and lubrication. This formed the subject of his Bakerian Lecture to the Royal Society in 1925. He resurrected a law, first put forward by Amontons as long ago as 1699, to the effect that in external friction the resistance to relative motion is independent of the area of the applied surfaces and varies directly with the force or load which presses them together. Experiments with a very large number of substances showed that the static friction is independent of the manner in which the lubricant is applied and of the quantity present, provided there is sufficient to form a primary film over each face. With a spherical slider on a plane surface Amontons's law was found to hold for a fifty-fold increase of load. The value of the coefficient of friction was found to be a function of two variables, the nature of the solid face and the chemical nature of the lubricant. Within the same chemical series it was found to be a linear function of the molecular weight and to decrease as the molecular weight increased.

IDA BIRCUMSHAW

REVIEWS OF BOOKS

Faraday (1791–1867), by THOMAS MARTIN (*Great Lives*, No. 40). Pp. 144. (London: Duckworth and Co., Ltd.) 2*s.* net.

Mr Martin is well known as Secretary of the Royal Institution and as Editor of the Faraday *Note-Books*; writing with a refresher from the Faraday papers in the custody of the Institution, he now presents in this volume a fascinating, all too brief account of the philosopher's life. The book is one to have and to hold; if books of worth were in demand at the bookstalls, it would be upon them all and freely read by the intelligent. A more elevating life is not to be found—upon no other model can we better shape our future action.

Huxley and others have talked of catching "potential Faradays" through technical education—can it be done? What would they give us? If the public have no measurement sense for money values—President Roosevelt shows this—how shall it evaluate mental and moral worth? How are we to measure the value of the man who first made electricity work—whose barely seen electromagnetic induction spark of 1831 holds the world in thrall to-day? Now endlessly enlarged, if it does not serve to move mountains, it thriftily uses their slopes by making the running waters of the world everywhere the servant of man, so putting the countries without storage of sunshine on a par with those that depend upon combustible fuel. Oil may come and oil may go, but rivers will run for ever: so long as they do, we may count upon living in amber security.

Faraday's name, however, is little known in the schools and unmentioned in pulpits. Even electricians have little thought of his work: they are content to enlarge his spark. By common consent, says Mr Martin, he is one of the great figures in English science. Who cares for such figures? The schools worship only those of antiquity. Faraday is far more than a great figure: taking into account both the ethical example of his life and his specific work as a discoverer, weighing works against words, we are justified in rating him *the greatest figure* in modern times and no such figure could exist previously. We have yet to secure for him his right place in society to give him a popular value.

Whatever impetus he may have given to the art of experimental inquiry, the worth of the spiritual example he set by his manner of working, studied in detail, is of far greater account—if only we will take it to heart—if there be enough of greatness in us to value the great. Probably the most weighty lecture ever delivered at the Royal Institution is that which Faraday gave, on May 6, 1854, before his Royal Highness, the Prince Consort of Queen Victoria—a most worthy listener—*On Mental Education*. It is printed in the volume of his collected papers on Chemistry and Physics. A better title would have been *On the Formation of Proportionate Judgment*. The doctrine set out in the lecture is embodied in his own early definition of the "natural philosopher," the term by which he preferred to be known. This Mr Martin quotes, as follows:

> The philosopher should be a man willing to listen to every suggestion but determined to judge for himself. He should not be biased by appearances; have no favourite hypothesis; be of no school and in doctrine have no master. He should not be a respecter of persons but of things. Truth should be his primary object. If to these qualities be added industry, he may indeed hope to walk within the vale of the temple of nature.

Some day we shall evolve from this lecture a few special commandments, a catechism and a set of collects, to be learnt and recited daily in schools: then inklings of scientific method may begin to dawn in the mind of the community. We have passed from the Iron

Age into the Amber Age through Faraday's act. Seeing that he has done so much to lead the world into communication and to carry us about by rail- and tram-way, maybe the public will eventually be led to take as much interest in his life as it now does in a Test Match or in the life of a deceased Prime Minister, even in the tales told by a Prime Minister's wife. To this end, someone has to write a real book around the man and his work, up to say the end of the fifth series of experimental researches (June 1834). Such a work might be made of the greatest educational value, in laying electro-chemical foundations.

Can Faraday be "explained"? Mr Martin's reading is scarcely satisfactory; he begins his book by saying:

> The mystery of heredity, the difficulty of finding in parents any evidence of the qualities of their children, was never better exemplified than in the birth and parentage of Faraday. His life's work was one of the most astonishing outpourings of natural genius the world has ever seen...his kingdom of natural philosophy was his by right of conquest and not by inheritance. His powers of intellect were his own. His family history shows no trace, among immediate forbears, of any predisposition to science or of intellectual attainment in any direction above the ordinary. Nor did he owe anything to training of the orthodox kind. His parents were poor and unable to give him any advantages in schooling. He was almost entirely self-taught. His education and scientific training followed no regular plan but were the outcome of his own interest in scientific things and desire to escape from trade and follow a scientific calling. It cannot even be said that he owed much to the example of others.

As to heredity—his father was a blacksmith and his uncles were all practical men: one a farmer, another a grocer, a third a shoemaker; his mother was a farmer's daughter; his elder brother a blacksmith who became a gas-fitter when gas was introduced as an illuminant: to-day he would have taken up electrician's work and wireless. His relations were therefore practical people: they had fingers and all took up independent careers, above the ordinary. Surely, we may regard both smithing and farming as sciences of a high order—the best of stock upon which to graft the desire to know: apparently, Faraday's early characteristic. As an apprentice he showed a desire to use both his fingers and his eyes, spending much time in drawing and showing no slight appreciation of graphic art. The sketches in his note-books, as Mr Martin points out, are evidence of his skill.

Leaving school at thirteen, he began to carry round newspapers. A year later, he was apprenticed as a book-binder. He thus learned to work and bound books not only in boards but into himself—he became an avid reader and had good books to read. For some reason undisclosed he had an inquiring mind; this was his making: it is probably the one essential to success in all walks of life. The modern boy of his age has little practice with his fingers and leads a lotus life at school, constantly tutored and confined in his outlook by the need of passing this and that examination. The inquisition of school and university is now such as to deprive boys and girls of all sense of freedom of thought. The idea that they must reach a high standard of verbal proficiency in this, that and the other subject—the neglect to develop faculty—the low standard of practical teaching and entire disregard of the soil—these together rip soul and individuality out of the great majority. We ruin the potential Faradays.

Faraday may be said to have been peculiarly happy in his early schooling, and his training after he entered Davy's service was ideal—a prolonged course in the art of pure discovery. Not only did Davy take him abroad and introduce him to the great workers of the day, but he set his assistant a wonderful example—by studying on his travels, in his bedroom, the new substance put into his hands in Paris, and at the end of a week recognizing in it a new element, which he named "iodine." Then, by using the great lens at Florence, he burned the diamond, for the first time, in oxygen, proving it to be carbon. Later came the discipline of the experiments which led to the safety lamp. Faraday must have participated in Davy's joy of discovery: we can be sure that the master was never reticent in the display of his satisfaction.

Nevertheless, he developed but slowly as an independent worker. His first serious experimental work—that on alloys of iron, only recently disclosed by Sir Robert Hadfield—was not begun until 1818. His first prolonged philosophical inquiry was that involving the comparison of electricities and the study of electrolytic phenomena, begun in 1831, and lasting until June 1834. In other words, he was full forty years old by the time he had felt his way into his subject and made himself a finished, logical worker. His notebooks show that he had an infinite capacity for taking pains: herein lay his genius. He had the inestimable advantage of being a pioneer, for the most part in an open field, unprejudiced by any great burden of existing knowledge. The freedom he enjoyed, coupled with his great obstinacy of purpose, accounts for a large measure of his success.

Out of scientific bounds, he was intensely prejudiced by home training. In his day, youth was brought up severely on Sundays. The Faradays were a religious family, members of a peculiar sect, the Sandemanians (Glasites), a body which accepted the Bible literally. Faraday held this faith and apparently without question: this is the more remarkable, as he was without mathematical bias and unable to let anything be granted without proof—witness the experiments on "table turning."

Owing to the continued retention in our schools and universities of ecclesiastical methods, doctrine and dogma are now almost universally taught and freedom of thought comes only to the few. The fact is, much as we know, we are unable as yet to overcome our human nature—man's infinite gullibility and clerical fixity of mind.

The present state of society—the world dominance of mechanism rather than of mind—would seem to be due to our failure to develop the sense of proportionate judgment, upon which Faraday laid such stress, as well as to the never ceasing indoctrination of dogma.

H. E. ARMSTRONG

Planetary Theory, by ERNEST W. BROWN and CLARENCE A. SHOOK. Pp. xii + 302. (Cambridge University Press). Price 15*s*. net.

Prof. Brown is pre-eminent among living authorities on celestial mechanics, and this volume, which he has written in collaboration with a distinguished fellow-worker in the same field, is not only a very important addition to the rather limited range of modern textbooks available for the student, but also a valuable contribution to the original literature of the subject. The authors have not set out to write a general treatise on dynamical astonomy or an exposition of the chief classical developments of planetary theory, but have in the main restricted themselves to giving a full and detailed account of two principal modes of procedure. Of these, one employs the method of changing the variables to elliptic elements and is analogous in its principles to Delaunay's method in lunar theory; the other is a planetary theory in which the orbital true longitude is used as independent variable; some account of this method, less well adapted for the novice, has already been published by Prof. Brown in *Monthly Notices*.

A preliminary derivation of the equations of motion is followed by a chapter devoted to theorems on formal expansions, especially in connection with Fourier series. This chapter may well be found useful for reference by many others than workers in this particular subject. The various series required in the discussion of elliptic motion are the main topic of the third chapter, and the next is occupied with the development of the disturbing function. What may be regarded as the preliminary part of the treatment is completed by a lucid introduction to the theory of canonical variables. The rest of the book deals at some length with the two principal methods referred to above, and concludes with two important chapters on resonance and on the Trojan group of asteroids respectively. Ten of these asteroids are now known, all discovered during the last thirty years; their motions approximately realize, in association with the sun and Jupiter, the equilateral-triangle solution of the problem of three bodies whose existence was pointed out by Lagrange. The theory of these motions presents special difficulties and constitutes one of the most interesting problems with which dynamical astonomy has had to deal in recent years. The chapter on resonance includes a valuable short discussion of general principles, but naturally the authors are chiefly concerned with the examples which present themselves in the solar system. There is a short appendix on numerical harmonic analysis.

The whole book abounds in those critical and explanatory comments, on both principles and details, with which a master of his subject elucidates not only what he is doing but why he is doing it. Celestial mechanics has long been displaced from its former dominant position in mathematical curricula, but it is a pity that it is so much neglected in modern university courses; its triumphs constitute some of the most remarkable achievements of the human mind, it still presents great and fascinating problems for solution, and its study provides a valuable mathematical discipline. The student who works through these three hundred pages will certainly find his labour profitable, even if he carries his purely astronomical reading no further. G. S. L.

Loud Speakers, Theory, Performance, Testing and Design, by N. W. McLachlan, D.Sc., M.I.E.E. Pp. xii + 399. (Clarendon Press, Oxford.) Price 40*s*. net.

This volume forms the third of the Oxford Engineering Science Series, and the author, who has made many original contributions to the subject, is a well-known authority on the design of loud-speakers. It is of interest to observe that the design of a good loud-speaker requires both scientific and engineering knowledge to no small degree—the fundamental principles of acoustics and alternating current engineering are intimately involved. It is not inappropriate therefore that this volume should be included in an "Engineering Science" series.

So much has been written about loud-speakers in a loose and popular style that it is indeed a pleasure to welcome a treatise which demands more serious consideration. A large amount of reliable scientific information has been published from time to time in this country, in America, and on the Continent, but such information has been almost obscured by the much greater volume of popular literature. British research-workers have done excellent work and Dr McLachlan himself is in the forefront. It is appropriate, therefore, that he should be the one to undertake the formidable task of collecting the scattered literature and combining it into a treatise which gives a well-balanced account of the whole subject. The author has not only done this, but has also filled in gaps by his own unpublished work.

The contents of the volume fall naturally into two parts. Chapters 1 to 12 deal with the analytical acoustical theory, i.e. the "scientific" side of the subject, whilst chapters 13 to 29 are concerned mainly with practical design and testing, i.e. the "engineering" aspect. For a thorough understanding of the theoretical section the reader will require a good mathematical knowledge, especially in regard to the use of Bessel functions; in the practical section of the book a working knowledge of the principles of alternating-current engineering is helpful, though perhaps not essential.

The theoretical section opens with a list of definitions and a brief outline of the fundamental principles relating to the radiation of sound. Following this, a number of chapters deal with the vibratory properties of diaphragms, conical shells, and rigid pistons. An important chapter relates to the spatial distribution of sound and the sound-power radiated from vibrating surfaces. Rayleigh's theory of the piston source has been extended considerably, and an original contribution by the author derives the variation of pressure over the surface of a rigid disc. The theory of moving coil and electrostatic loud-speakers is given in considerable detail, not to be found elsewhere in the general literature of the subject. The theory of horns is treated very thoroughly, and the analytical section of the book concludes with chapters on sound waves of finite amplitude and on transients.

The technical section is concerned with the more important factors influencing the design, test, and construction of loud speakers. Driving mechanisms, magnets, efficiency, electrical impedance measurements, response curves, vibrational frequencies of conical shells, form the basis of succeeding chapters. These are followed by two important chapters on the design of hornless and of horned moving-coil loud-speakers. Numerous references to scientific literature relating to the subject are collected and conveniently arranged under subject titles, at the end of the book.

Dr McLachlan's treatise may be heartily recommended for study not only by electrical and acoustical engineers for whom it is primarily designed, but also by scientists who are more generally interested in the mathematical theory of sound and who may or may not be directly interested in the design of loud-speakers. Teachers and students will find a wealth of theoretical subject-matter of a novel kind which will repay serious study.

The book is well written in a clear style which will make a general appeal. Dr McLachlan deserves congratulation on his success in compiling such a volume, and the Oxford University Press on the selection of the author.

A. B. W.

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CAMBRIDGE: PRINTED BY WALTER LEWIS, M.A., AT THE UNIVERSITY PRESS